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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

NO. II.

THE ACTION OF BROMINE ON TOLUOL, AND SOME OF ITS DERIVATIVES.*

BY C. LORING JACKSON AND A. W. FIELD.

The history of the action of halogens on toluol begins with the discovery of toluol by Pelletier and Walter, who say in their paper,† published in 1838, on "retinnaphte" (toluol) from coal tar, that by distilling it repeatedly in a stream of chlorine there was formed a brownish-yellow oil with a sharp taste, a very strong smell somewhat like that of horse-radish, and a powerful action on the eyes, whose formula, founded on a doubtful analysis, was $C_7H_6Cl_2$, and which with potassic hydrate gave potassic chloride and an oil with a different smell. They also tried the action of bromine on boiling retinnaphte, and made in this way a compound similar to the preceding in every respect, but they observed that the cold hydrocarbon was apparently unaffected by chlorine.

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* Presented to the American Academy of Arts and Sciences. Communicated by the Authors.

† Ann. Chim. Phys. 67, 269.

Deville* was the next to take up the subject in 1841, in his paper on balsam of tolu, from which he obtained a hydrocarbon (benzoene) identical with the retinnaphte of Pelletier and Walter. From this he made the following compounds: C_7H_7Cl, boiling point 170°, by the action of chlorine on the hydrocarbon when cooled and protected from light; $C_7H_6Cl_4$ in diffused daylight; $C_7H_5Cl_7$ when the chlorine was in excess; $C_7H_6Cl_8$ in direct sunlight; and $C_7H_2Cl_6$ by repeated distillation in an atmosphere of chlorine.

The next important step was taken by Cannizzaro† in 1855, who proved that the product of the action of chlorine on toluol is identical with benzylchloride made from benzylalcohol. Beilstein,‡ in 1860, introduced a great deal of confusion into the subject by contradicting Gerhardt's§ inference from Deville's work, that the action of chlorine on cold toluol was different from its action on hot, and describing experiments of his own to prove that differences in temperature made no difference in the products. He also thought he had proved the identity of the dichlortoluol from toluol and chlorine with the chlorobenzol made from benzaldehyde with phosphoric pentachloride, but Cahours,‖ three years later (1863), announced that they were only isomeric. In the same year (1863), Naquet¶ studied trichlortoluol in comparison with the product of the action of phosphoric pentachloride on benzylchloride.

The next important discovery was made in 1865 by Fittig and Glinzer,** who obtained monobromtoluol by treating cold toluol with bromine, and pointed out the marked differences between it and chlortoluol (benzylchloride); while in 1866 Kekulè,†† in his paper on aromatic isomeres described benzylbromide made from benzylalcohol, and, after comparing it with monobromtoluol, explained the cause of their difference.

In this same year (1866), Beilstein, in conjunction with Geitner,‡‡ put the whole subject on a firm basis by the following statement, since known as *Beilstein's Law:—Toluol behaves differently with chlorine according as it is hot or cold;* in the cold, a chlortoluol as stable as chlorbenzol is formed, usually, however, mixed with benzylchloride unless great care is taken in cooling. If hot, the toluol is converted into benzylchloride, but it is not necessary absolutely to boil it, as a very slight increase of temperature is enough com-

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* Ann. Chim. Phys. ser. 3, 3, 178.

† Ann. Chem. Pharm. 96, 246.

‡ Traité de Chimie, 3, 567.

§ Ibid. 116, 336.

‖ Comptes rendus, 56, 222.

¶ Ibid. 55, 407; 56, 129.

** Ann. Chem. Pharm. 133, 47; 136, 301.

†† Ibid. 137, 188.

‡‡ Ibid. 139, 331.

pletely to prevent the formation of chlortoluol. *With iodine only chlortoluol is formed under all conditions, even when the toluol is boiling*;[*] the chlortoluol obtained by this process is however contaminated with substances containing iodine. In this paper they predict a similar action with bromine, and state that xylol behaves with chlorine like toluol. A paper by Limpricht[†] in the same volume of the *Annalen der Chemie und Pharmacie*, and another by Cannizzaro[‡] in the next volume but one, did not advance the subject materially.

Lauth and Grimaux[§] in 1867, described a convenient form of the process for making benzylchloride, consisting in passing chlorine into toluol heated to 110–140° in a flask with a return condenser. In the same year, Beilstein[||] extended his law to the action of bromine on toluol, which, if iodine was present, gave bromtoluol as the only product with the exception of a little of some iodine compound, even if the toluol was boiling, while without iodine bromine formed with boiling toluol benzylbromide, always, however, mixed with some bromtoluol. Lauth and Grimaux,[¶] on the other hand, could find no bromtoluol in the product obtained by mixing the vapors of bromine and toluol.

Since that time but little progress has been made in this subject, the papers in which the action of halogens on toluol is mentioned dealing rather with the products than with the conditions of the action, but the following papers deserve mention: Fittig,[**] on the formation of bromtoluol free from benzylbromide; Beilstein and Kuhlberg,[††] extending Beilstein's Law to the action of chlorine on the various chlorine compounds of toluol, and one of their later papers[‡‡] (on tetrachlortoluol) in which they direct that 2 or 3 grams of iodine should be used to make the chlorine enter the ring. This is the only statement of the amount of iodine needed for this purpose that we have been able to find, and even here nothing is said of the amount of toluol to be used with the 3 grams of iodine.

We have not been more successful in finding definite statements about the temperature at which the bromine begins to enter the side-chain. Those authors[§§] who mention any temperature give the

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[*] The use of iodine was suggested by the paper of H. Müller (Journal London Chem. Soc. 15, 41) on making chlorine substitution products from benzol in presence of iodine.

[†] Ann. Chem. Pharm. 139, 303. [‡] Ibid. 141, 198. [§] Ibid. 143, 79. [||] Ibid. 143, 369.

[¶] Bull. Chem. Soc. 7, 108. [**] Ann. Chem. Pharm. 147, 39.

[††] Ibid. 146, 317; also 147, 339. [‡‡] Ibid. 150, 286.

[§§] Vogt and Henninger, Ann. Chim. Phys. ser. 4, 27, 130. Grimaux Comptes rendus, 70, 1363. Radziszewski, Ber. d. ch. G. 1873, p. 492.

boiling point of the substance to be acted on, or a temperature somewhat above this, with the exception of Wachendorff,* who in studying the action of bromine on para- and metanitrotoluol, found that the benzylbromine was formed as low as 130° in a sealed tube, or at 180° in open vessels, while at its boiling point the nitrotoluol was almost entirely decomposed by bromine.

In the work described in this paper we have tried to give a more definite statement to Beilstein's law,—which may be stated thus: When toluol (or its derivatives) is treated with chlorine or bromine in the cold, the halogen attaches itself to the benzol ring; if hot, to the side-chain; in presence of iodine exclusively to the ring, even when boiling.—To do this we have tried to determine the amount of benzylbromide formed from toluol and some of its derivatives, in the first place at different temperatures, and secondly in presence of different amounts of iodine.

Effect of Differences in Temperature.

In these experiments a weighed amount of toluol or the substituted toluol was heated in a flask with a return condenser by a paraffine bath, and the calculated quantity of bromine added with a drop-funnel at such a rate that no bromine could be seen in the fumes which escaped through the condenser. The temperature of the bath and of the vapor within the flask was noted throughout the experiment. To determine how much benzylbromide had been formed we used the following method, which is very similar to that used by Cannizzaro† for the same purpose. The product of the reaction, after being freed from hydrobromic acid by washing first with a dilute solution of sodic carbonate and afterwards with distilled water, was heated to 100° with alcoholic ammonia for two hours; the bromides of ammonium and the three benzylamines thus formed were decomposed by warming with a solution of baric hydrate, and the amount of baric bromide determined by Volhard's‡ sulphocyanate method of titration after the organic matter had been filtered off. To test the method of estimating the amount of removable bromine, pure parabrombenzylbromide was treated with alcoholic ammonia and baric hydrate, as described above, and 98 per cent. of the calculated amount of bromine obtained. The experiments collected in Table I. were then made.

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* Ann. Chem. Pharm. 185, 259.

† Ibid. 141, 198.

‡ Ibid. 190, 1.

TABLE I.

ACTION OF BROMINE ON TOLUOL. BOILING-POINT, 111°.

Number of Experiment.	Amount taken.	Temperature.		Per cent. of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
I.	5 grs.	100°	97°-98°	72.	65
II.	5 grs.	100°	98°-100°	54.	20
III.	10 grs.	100°	97°-98°	55.	60
IV.	10 grs.	100°	95°	65.	55
V.	5 grs.	120°	110°-114°	82.	10
VI.	10 grs.	120°	112°-114°	87.	20
VII.	10 grs.	120°	111°-113°	74.	20

ACTION OF BROMINE ON PARACHLORTOLUOL. MELTING-POINT, 7°; BOILING-POINT, 160°.

Number of Experiment.	Amount Taken.	Temperature.		Per cent of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
VIII.	6.9 grs.	100°	81°-86°	69.	45
IX.	"	120°	110°-113°	80.	
X.	"	140°	130°-135°	92.	20
XI.	"	167	157°-161°	95.	15

ACTION OF BROMINE ON PARABROMTOLUOL. MELTING-POINT, 28.5°; BOILING-POINT, 185°.

Number of Experiment.	Amount taken.	Temperature.		Per cent. of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
XII.	9.4 grs.	100°	87°-92°	51.	
XIII.	"	100°	90°-93°	58.	40
XIV.	"	120°	111°-114°	95.	25
XV.	"	120°	110°-114°	90.	30
XVI.	"	140°	130°-134°	88.	10
XVII.	"	170°	160°-164°	92.	8
XVIII.	"	190°	180°-184°	94.	5

ACTION OF BROMINE ON ORTHOBROMTOLUOL. BOILING-POINT, 182°.

Number of Experiment.	Amount taken.	Temperature.		Per cent of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
XIX.	9.4 grs.	100°	90°	21.	30
XX.	"	100°	86°-92°	31.	45
XXI.	"	100°	90°	32.	55
XXII.	"	1 0°	110°-114°	74.	50
XXIII.	"	140°	130°-134°	83.	25
XXIV.	"	170°	160°-164°	84.	10
XXV.	"	190°	180°-184°	84.	15

Before considering the inferences which can be drawn from these results, it is necessary to examine the sources of error which affect the accuracy of the process; and, for this purpose, all the results obtained under the same conditions are collected in Table II.

TABLE II.

No. of Experiment.	Time in Minutes.	Per cent.
Toluol at 100°.	5 grs. used.	
I.	65	72
II.	20	54
Toluol at 100°.	10 grs. used.	
III.	60	55
IV.	55	65
Toluol at 120°.	5 grs. used.	
V.	10	82

No. of Experiment.	Time in Minutes.	Per cent.
Toluol at 120°.	10 grs. used.	
VI.	20	87
VII.	20	74
Parabromtoluol at 120°.		
XIV.	25	95
XV.	30	90
Orthobromtoluol at 100°.		
XIX.	30	21
XX.	45	31
XXI.	55	32

The want of agreement between these results can be ascribed to two causes: first, differences in the rate of adding the bromine; second, unavoidable defects in the method of bromiring or of treating the product. To the first class belong the difference of 18 per cent., corresponding to 45 minutes difference in rate between Nos. I. and II., and that of 10 per cent., corresponding to 15 minutes between Nos. XIX. and XX.; but these are the only differences that come under this class, a difference of less than 10 minutes having apparently no effect upon the amount of benzylbromide formed (see XX. and XXI.). The differences due to the second cause are that of 10 per cent. between III. and IV., 13 per cent. between VI. and VII., and 5 per cent. between XIV. and XV., which show that our method is incapable of giving the exact quantitative results that we had hoped for. The most probable cause of these variations is the difficulty of washing and handling the liquid or pasty product of the bromiring. In the following discussion, Experiment I. will be rejected, because of the very slow rate at which the bromine was added, and differences of less than 10 per cent. will be accepted, if at all, only with greatest caution.

Effect of the Temperature on the Amount of Benzylbromide formed.—To make this comparison easier, the results given in

Table I. (reduced to the mean where there are several observations at the same temperature) are collected in the following table, and in the second column, under each substance, the differences between the percentages at each temperature, and at that which immediately follows it, are given.

TABLE III.

Temperature.	Toluol.		Parachlortoluol.		Parabromtoluol.		Orthobromtoluol.	
	Per cent.	Difference.	Per cent.	Difference.	Per cent.	Difference.	Per cent.	Difference.
81°–100°	58		69		54		28	
		23		11		38		46
110°–114°	81		80		92		74	
				12		—4		9
130°–135°			92		88		83	
				3		4		1
160°–164°			95		92		84	
						2		0
180°–184°					94		84	
110°–Bpt.				15		2		10

From this it appears that the bromine begins to enter the side-chain in considerable quantity at about the boiling point of toluol (111°), and that after this the amount of benzylbromide formed increases with the temperature, although to a much smaller extent, with the exception of parabromtoluol, which is probably due to defects in the process; in fact, the difference between 81°–100° and 110°–114° is greater than that between the latter temperature and the boiling point of the substance, except in the case of the single series of observations on parachlortoluol.

Some experiments with paraiodtoluol cannot be directly compared with the preceding, because we could find no satisfactory way of removing the iodine set free during the addition of the bromine, and were therefore obliged to content ourselves with weighing the crystals of paraiodbenzylbromide formed. We found, under these conditions, that below 100° no crystals were formed; at about 111°, 18 per cent. of the calculated amount was obtained; at 135°, 42 per cent.; at 175°, 54 per cent.; at 200°, 51 per cent. The low percentages are partly accounted for by the solubility of the paraiodbenzylbromide in the oily secondary products. A similar series with parachlortoluol gave below 100° no crystals; at 111°, 89 per cent. of very impure crystals (apparently nearly one-half parachlortoluol); at 135°, 98 per cent. of purer crystals; at 160°, 89 per cent. These results confirm, in a general way, those obtained by the more accurate method.

The effect of differences in temperature on the rate at which the bromine is taken up will be seen from the following table, in which the mean time needed to convert into the bromine product equivalent weights of the substances for each temperature is given. In calculating these means, the times of several experiments were used, in which the amount of benzylbromide was not determined; many of them, therefore, depend on a much larger number of observations than the mean amounts given in Table III.

TABLE IV.

Temperature.	Time in Minutes.			
	Toluol.	Parachlortoluol.	Parabromtoluol.	Orthobromtoluol.
81°–100°	26	40	43	43
110°–114°	11	30	27	40
130°–135°		22	10	25
160°–164°		20	8	10
180°–184°			5	15

Although the method of adding the bromine used by us made great differences of rate, under the same conditions, possible, so that all these results must be taken with some caution, it is evident that the rate increases rapidly, and apparently regularly, with the temperature, showing no especially large increase between 81°–100° and 110°–114°, as was the case with the per cent. This rapid increase in the rate suggests the following objection to the results obtained in studying the effect of temperature on the amount of benzylbromide formed; the small percentages of benzylbromide obtained below 100° may have been due to loss of bromine from running the experiment too fast, as the secondary products were not studied; and therefore it is possible that they were the unaltered original substance, and not formed from this by substitution of bromine in the ring; this view is supported by the larger per cent. (72) obtained in Experiment I., where the time was 45 minutes longer than in II.; but, on the other hand, it is hardly possible that nearly 5 grams of bromine could have escaped without giving a perceptible color to about the same quantity of hydrobromic acid, and great pains were taken in every experiment to regulate the addition of the bromine so that the escaping fumes should be perfectly colorless. Even if the amounts of benzylbromide obtained below 100° are rejected on this account, our statement that there is a decided change in the action at 111° still holds good, as in that case the time necessary to take up the bromine below 100° must be greatly increased, and therefore the differences in rate between 87°–100° and 110°–114° would become as great in proportion to the differences between other temperatures as those in the percentages are if our present results are accepted.

We had hoped, in beginning this research, to make a careful comparison of the action of bromine on toluol and its substitution products, but the differences between the results from different substances fall so near the wide limits of error of our process, that we prefer to confine ourselves to the following very general statements. Bromine is taken up by toluol more rapidly than by any of its substitution products studied; orthobromtoluol seems to take up bromine less rapidly than parabromtoluol, and this inference from our quantitative results is confirmed by our experience in the preparation of the substituted benzylbromides in large quantity, when it has been observed invariably that the parabromtoluol absorbed bromine most rapidly, the meta-compound less so, and the orthobromtoluol even more slowly than the meta. In regard to the percentages of benzylbromide formed from each substance we do not feel that our results allow us to make any generalization, as the apparently lower numbers obtained from the orthobromtoluol may be due to differences in working up the product, which in the case of the ortho-compound is a liquid, while the parabromtoluol yields a pasty solid.

We have also tried some experiments with toluol at lower temperatures, and found that at 58°, and even at 0°, a small amount of benzylbromide was formed, as shown by obtaining an amine on treatment of the product with alcoholic ammonia. The rate at which the bromine was taken up was, however, extremely slow, and we feel that these experiments need confirmation.

Effect of the Addition of Iodine.

We were induced to take up this branch of the subject by the observation that paraiodbenzylbromide was formed by the action of bromine on paraiodtoluol, even when the flask was filled with violet vapors of iodine during the addition of the bromine, which contradicted Beilstein's Law as generally understood; but we have not studied it so thoroughly as the effect of differences in temperature, as we could find no sufficiently satisfactory and easy method of determining the amount of benzylbromide formed.

Our best series of results (Table V.) was obtained from parachlortoluol treated with bromine at 160°, the crystals of parachlorbenzylbromide formed being weighed after they had been brought to the melting point of the pure substance, 48.5°.

TABLE V.

Per cent. of Iodine added.	10 grs. Parachlortoluol yielded.	Per cent of possible Amount.
1	6.5 grs.	51
5	3. grs.	23
10	No crystals.	

The product of the last experiment was washed, boiled with alcoholic sodic acetate, and then heated in a sealed tube with aqueous ammonia, when crystals of the parachlorbenzylalcohol were obtained, showing that even in presence of 10 per cent. of iodine a portion of the bromine enters the side-chain. This result was confirmed by some experiments on toluol, in one of which toluol was mixed with 10 per cent. of iodine and treated with chlorine at 120°; on fractioning the product, about one-half passed over from 164°–222° (chlortoluol boils from 156°–160°), attacked the mucous membrane of the nose violently, and gave an amine when heated in a sealed tube with alcoholic ammonia; it must, therefore, have contained benzylchloride (boiling point 176°), and probably chlorbenzylchloride (boiling point 213°). In another experiment it seemed that even 40 per cent. of iodine was not enough to completely prevent the formation of benzylbromide at 111°; but the determination of the benzylbromide by the amine process was interfered with by the presence of iodine substitution products to such an extent that we can place but little reliance on this result.

Summary.

I. The portion of Beilstein's Law which states that benzyl-compounds are formed at high, and substituted toluols at low temperatures, is confirmed by our experiments.

II. The benzyl-compound begins to be the principal product near the boiling point of toluol (111°); in other words, no connection can be traced between the boiling point of a substituted toluol and the temperature at which the bromine begins to enter its side-chain in quantity. Above 111° there is a gradual increase in the amount formed as the temperature is raised; but the total increase from 111° to the boiling point of the substance is usually smaller than the increase from 100° to 111°.

III. The rate at which the bromine is taken up becomes more rapid as the temperature is raised.

IV. Toluol takes up bromine more rapidly than its substitution products. This result is confirmed by the observation of Beilstein and Kuhlberg,* that the more chlorine there was attached to the ring, the harder it was to introduce chlorine into the side-chain.

V. The monobromtoluols seem to take up bromine (in the side-chain) in the following order: para most rapidly, meta next, ortho least rapidly.

VI. The portion of Beilstein's Law which states that in presence of iodine no benzyl-compound is formed, even at the boiling point, is not true when the amount of iodine is 10 per cent. or less, and it is probable that toluol yields a little benzylbromide at 111°, even in presence of 40 per cent. of iodine.

From our experiments it follows that the best way to obtain a benzylbromide is to add the bromine at the boiling point of the substance used, but it is not well to allow the temperature to rise above this point, as then there is danger of decomposition of the product.

ON α- AND β-MONOBROMCROTONIC ACIDS.

By Arthur Michael and Lewis M. Norton.

Aug. Kekulè,† in his researches on non-saturated organic acids, found that citradibrompyrotartaric acid when heated with an aqueous alkaline solution decomposed, forming carbonic, hydrobromic and a monobromcrotonic acid, and that the latter acid gave on reduction with nascent hydrogen butyric acid. A short time

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* Ann. Chem. Pharm. 150, 286.

† Ann. Chem. Pharm. Suppl. 2, 97.

later, A. Cahours* obtained, by the action of bromine on potassium citraconate, a dibrombutyric acid, which on boiling with alkalis decomposed into hydrobromic and the bromcrotonic acid of Kekulè. It is evident that these acids are of the greatest importance in ascertaining the constitution of citraconic acid, and with this object in view W. Körner† endeavored to obtain them synthetically from solid crotonic acid, by subjecting it to the action of bromine, and treating the dibrombutyric acid thus formed with alkalis. Körner only published a preliminary notice of his results, in which he states that the monobromcrotonic acid thus obtained is in every respect identical with the acid of Kekulè. Bulk‡ has also examined the action of bromine on solid crotonic acid, and obtained a solid compound which he considered as either dibromcrotonic or -butyric acid; his analytical results indicate the formation of the first compound. It would appear from the results obtained by Kekulè and Körner that the bromo-acid is a derivative of solid crotonic acid, but the later investigations of Geromont§ and Swarts,‖ who reduced this acid and found it yielded isobutyric acid, of Morawski¶ and of Fittig and Prehn** have shown that this conclusion is erroneous, and that it must be considered as a monobrommethacrylic acid. Körner's results, therefore, appear extremely interesting, since to explain the identity of the two monobromo-acids a molecular rearrangement of bromcrotonic into brommethacrylic acid must be supposed. We considered this subject of sufficient interest to repeat Körner's experiments, and examine his bromcrotonic acid more thoroughly.

β-Monobromcrotonic Acid.

This acid is the product of the action of alcoholic potash upon αβ-dibrombutyric acid.††

The dibrombutyric acid was obtained in the following manner: solid crotonic acid was dissolved in a large quantity of carbonic disulphide, and to this solution a solution of one molecule of bro-

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* Ann. Chim. Phys. [3] 67, 139. † Ann. Chem. Pharm. 137, 233. ‡ Ibid. 139, 68.

§ Deutsch. ch. Ges. Ber. 1872, 92. ‖ Bull. Acad. Belgique [2] 33, 1.

¶ J. prkt. Chem. [2] 12, 398. ** Ann. Chem. 188, 51.

†† We propose to call this acid the αβ-dibrombutyric acid, from the position of the two bromine atoms towards the carboxyl group. Tollen's dibrompropionic acid would therefore be the αβ-acid, and the name β-dibromo-acid, which he gave to this acid, would designate the hitherto unobserved third dibromo-acid in which the two bromine atoms are both in the β-position towards the carboxyl group. The bromcrotonic from the αβ-dibrombutyric acid is designated as the β-acid for reasons given below.

mine in the same solvent was gradually added. At first the color of the bromine disappeared rapidly; toward the end of the treatment more slowly. The mixture was allowed to stand twenty-four hours, and the carbonic disulphide then removed by distillation. The acid is easily soluble in alcohol, benzol and ether, and crystallizes from the latter solvent in long, white needles, which melt at 87°. It is but sparingly soluble in cold, more readily in hot water.

The bromine estimation of the pure acid yielded the following result:

		Calculated for $C_4H_6Br_2O_2$.	Found.
Br	...	65.04	65.30

The silver salt could not be obtained in a state of purity, owing to the ease with which it decomposes, with a separation of silver bromide. The yield of the dibrombutyric acid by the method described is almost the theoretical.

The β-monobromcrotonic acid was obtained by treating an alcoholic solution of the above described acid with an alcoholic solution of two molecules of potassium hydrate. When the solutions were mixed a slight increase in the temperature was noticed, and an immediate deposition of potassium bromide took place. The reaction was completed by heating the solution for a few minutes on a water-bath. The potassium bromide was then removed by filtration, the alcoholic solution diluted with eight or ten times its volume of water, made acid with dilute sulphuric acid, and then extracted with ether. Upon evaporation of the ether the monobromcrotonic acid remained as a mass of white crystals; these were recrystallized repeatedly from water until a constant melting point was reached. The analysis of the pure acid gave the following results:

		Calculated for $C_4H_5BrO_2$.	Found.
C	...	29.09	28.75
H	...	3.03	2.87
Br	...	48.48	48.61

The β-monobromcrotonic acid is easily soluble in ether, alcohol and carbonic disulphide, and tolerably soluble in hot water, from which it crystallizes in long, white needles.

The melting point of the pure acid, precipitated from the barium salt by the addition of chlorhydric acid and recrystallized, is 92°.

The silver salt was prepared from an aqueous solution of the ammonium salt by the addition of silver nitrate, and crystallizes in white needles. It is very stable toward light and quite insoluble in cold water.

		Calculated for $C_4H_4BrO_2Ag$.	Found.
Ag	...	39.66	39.42

The barium salt was obtained by neutralizing an aqueous solution of the acid with barium carbonate; the salt was subsequently crystallized from water. It crystallizes in plates and contains $3\frac{1}{2}$ molecules of water. It is easily soluble in water.

		Calculated for $(C_4H_4BrO_2)_2Ba + 3\frac{1}{2}H_2O$.	Found.
H_2O	...	11.93	11.39

The barium determination in the anhydrous salt gave the following result:

		Calculated for $(C_4H_4BrO_2)_2Ba$.	Found.
Ba	...	29.46	29.51

The calcium salt was obtained in a similar manner to that used for the barium salt. It is easily soluble in water and crystallizes in rhombic plates. The salt contains 3 molecules of water of crystallization.

		Calculated for $(C_4H_4BrO_2)_2Ca + 3H_2O$.	Found.
H_2O	...	12.55	12.69

The calcium determination in the anhydrous salt gave the following result:

		Calculated for $(C_4H_4BrO_2)_2Ca$.	Found.
Ca	...	10.87	10.41

By the action of sodium amalgam the β-monobromcrotonic acid was converted into the sodium salt of an acid which contained no bromine. The acid was separated, purified, and the salts examined. Its properties correspond perfectly with those of the normal butyric acid. The behavior of the calcium salt, and the solubility of the silver salt (1 part of the salt in 24 parts of water) leave no doubt that the acid is normal butyric acid.

The β-monobromcrotonic acid easily takes up one molecule of bromine, forming a tribrombutyric acid.

The monobromcrotonic acid was dissolved in carbonic disulphide and treated with one molecule of bromine also in solution in the same solvent. After standing twenty-four hours the carbonic disulphide was removed by distillation, and there remained a mass of white crystals. These were purified by recrystallization from benzol and analyzed with the following result:

		Calculated for $C_4H_5Br_3O_2$.	Found.
C	...	14.76	15.28
H	...	1.52	1.77
Br	...	73.84	74.07

The tribrombutyric acid is very soluble in alcohol and benzol, and crystallizes from these solvents in large, colorless rhombic plates which melt at 114° without decomposition. It is somewhat soluble in cold water, more freely in hot, but separates from the latter on cooling in the form of an oil which first becomes a solid when a crystal of the substance is brought in contact with it. The acid sublimes much below its melting point. We were unable to obtain salts of the acid in a pure state, owing to the ease with which they decompose, with the formation of a bromide.

If we compare the properties of the above-described bromcrotonic acid with those of Kekulè's brommethacrylic acid, and also of the tribromo-acids obtained from them by the addition of bromine, it will be seen that they are not identical in any respect, and it is therefore evident that Körner's observations were not correct. Furthermore, the reduction of the bromcrotonic acid to normal butyric acid shows conclusively that a molecular transformation has not occurred.

α–Monobromcrotonic Acid.

It became of interest to examine the action of bases on the liquid or α-dibrombutyric acid, and compare the monobromcrotonic acid thus formed with the acid above described. For this purpose a large quantity of dibrombutyric acid was prepared by heating butyric acid with two molecules of bromine in sealed tubes at 130°–140°. Its properties and boiling point corresponded with those given by Friedel and Muchuca.* The acid (one molecule) was dissolved in alcohol and treated with an alcoholic solution of two molecules of potassium hydrate. The action does not take place so easily as in the case of the αβ-acid, and is not completed without several hours heating with reversed condenser upon a water-bath. The potassium salt of the monobromcrotonic acid is easily soluble in alcohol, and the potassium bromide was separated by filtration. The alcoholic filtrate was then diluted with a large volume of water and acidified with dilute sulphuric acid, after which it was extracted with ether. The acid remained as a white crystalline mass, after

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* Compt. rend. 54, 220.

the distillation of the ether. It was purified by repeated crystallizations from water and analyzed with the following result:

		Calculated for $C_4H_5BrO_2$.	Found.
C	...	29.09	29.22
H	...	3.03	3.17
Br	...	48.45	48.78

The acid is somewhat soluble in cold water, much more so in hot, from which it crystallizes in long, colorless needles. It is easily soluble in alcohol, ether and benzol, more difficultly soluble in carbonic disulphide. It melts at 106.5°, and is partially decomposed upon boiling. The yield was very small, not exceeding ten per cent. of the amount required by the theory.

The silver salt was precipitated in the form of white needles from a concentrated aqueous solution of the ammonium salt by the addition of silver nitrate. It decomposes slowly in aqueous solution in the cold, with the deposition of silver bromide, very quickly by boiling the solution. The salt is exceedingly sensitive to the influence of light. The analysis gave results as below:

		Calculated for $C_4H_4BrO_2Ag$.	Found.
Ag	...	39.70	40.05

The barium salt was obtained by neutralizing an aqueous solution of the acid with barium carbonate, and was purified by recrystallization from water, in which it is quite soluble. It contains 2 molecules of water, and crystallizes in plates.

	Calculated for $(C_4H_4BrO_2)Ba + 2H_2O$.	Found.
H_2O	7.16	7.11

This monobromcrotonic acid is also obtained by treating the dibrombutyric acid with alcoholic ammonia. We noticed also the formation of the acid, when the α-dibrombutyric acid was heated nearly to its boiling point, fumes of bromhydric acid being given off at the same time.

To examine the action of bromine on the α-monobromcrotonic acid, it was dissolved in a large quantity of carbonic disulphide, and a solution of one molecule of bromine in the same solvent slowly added. After 24 hours the carbonic disulphide was removed by distillation, leaving a mass of white crystals behind. The acid was purified by recrystallization from alcohol, and the bromine estimation resulted as follows:

		Calculated for $C_4H_5O_2Br_3$.	Found.
Br	...	73.84	73.63

The acid separates from water, in which it is easily soluble, in bunches of white needles, which melt at 111°. It is also very soluble in alcohol, ether and carbonic disulphide. We were unable to obtain salts. We do not feel certain regarding the identity of this acid with the acid obtained by the action of bromine upon the β-monobromcrotonic acid. The small quantity at our disposal would not allow a full investigation and comparison, but so far as we are able to judge the acids are *not* identical.

Constitution of α- and β-bromcrotonic Acids.

The rational formula of α-bromcrotonic acid is dependent on that of α-dibrombutyric acid, in which the position of the second bromine atom has not been established, although judging from the action of bromine on other organic acids, the α-position would seem very probable. In this case the bromcrotonic acid obtained from it would have the formula $CH_3—CH = CBr—COOH$. Assuming this probable formula, there remains for the acid from αβ-dibrombutyric acid two possible formulae—$CH_3—CBr = CH—COOH$, and $CH_2 = CH—CBr—COOH$—of which the former is the more probable.

The formation of different bromcrotonic acids from α- and αβ-dibrombutyric acids presents considerable interest, as Tollens has shown that the α- and αβ-dibrompropionic acids yield the same bromacrylic acid. Our results, in thus characterizing an important difference in the properties of substitution products of propionic and butyric acids, indicate that a more thorough and systematic investigation than has hitherto been made of the substitution products of the fatty acids will show further marked differences in the properties of these acids; results which would contribute in no small measure to a better insight into the relations and nature of homologous organic compounds.

Tribrompropionic Acid.

The ease with which bromine adds itself to the above described monobromcrotonic acids indicates the possibility of a like action in the case of monobromacrylic acids, and led us to examine the behavior of bromine towards α-bromacrylic acid, an acid which has been so fully investigated by Tollens. We have modified the methods hitherto in use for the preparation of dibromallyl alcohol in such a manner as to very greatly increase the yield. The allyl alcohol was dissolved in portions of 20 grams each in 100 grams of carbonic disulphide, and a solution of 60 grams of bromine in 300 grams of carbonic disulphide was allowed to fall, drop by drop, into the solution of allyl alcohol, the latter being kept cool. The bromine is instantly absorbed, and there is a constant tendency to heating, which must be avoided as far as possible. The treatment of a portion of 20 grams should occupy some three to four hours. The carbonic disulphide is then removed by distillation and the dibromallyl alcohol purified by distillation *in vacuo.* The yield of pure dibromallyl alcohol, by this method, rises to 90 per cent. of the amount required by the theory. The dibromallyl alcohol was oxidized according to the method given by Tollens* to dibrompropionic acid and then converted into monobromacrylic acid by treatment with alcoholic potash, separated and purified as recommended by him.† Our observations on all these compounds agree very closely with his. Pure monobromacrylic acid crystallizes in large plates, which melt at 69°.

The process of obtaining the tribrompropionic acid was as follows: the bromacrylic acid was dissolved in a large quantity of carbonic disulphide, and to this solution a solution of one molecule of bromine in disulphide was slowly added. The color of the bromine disappeared rapidly at first, toward the end of the operation more slowly. After standing twenty-four hours the carbonic disulphide was removed by distillation, and there remained behind a very hygroscopic crystalline mass. This was quickly pressed between bibulous paper to remove any traces of carbonic disulphide, then crystallized twice from ether and finally once from benzol, after which the melting point remained constant at 92°. The analysis gave the following results, which correspond with the theoretical figures for tribrompropionic acid:

		Calculated for $C_3H_3Br_3O_2$.	Found.
C	...	11.57	11.50
H	...	.96	1.28
Br	...	77.17	77.25—77.13

The tribrompropionic acid is sparingly soluble in cold water, somewhat more soluble in hot water, from which it separates as an oil which remains liquid as long as it contains a trace of water. A drop of water placed upon the pure acid instantly converts it into

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* Ann. der Chemie, 171, 341 (note).

† Wagner and Tollens, Ann. loc. cit.

an oil. The acid is not hygroscopic when perfectly pure. It is very easily soluble in alcohol and ether, more difficultly soluble in benzol, from which it crystallizes in beautiful needles. The melting point of the pure compound is 92°, but a small mixture of impurities lowers it in an extraordinary degree. The rational formula is $CH_2Br—CBr_2—COOH$.

We were unable to examine the salts of this acid. The silver salt appears to be exceedingly unstable. The barium and strontium salts are more permanent, but we were unable to obtain them in a state suitable for analysis: they are both very soluble in water. If the tribrompropionic acid is treated with two molecules of potassium hydrate in alcoholic solution, the liquid immediately becomes warm and potassium bromide separates. The solution contains the potassium salt of an acid, which is apparently a dibromacrylic acid.

This tribrompropionic acid does not appear to be identical with the one obtained by Fittig and Petri* by the action of bromhydric acid upon dibromacrylic acid. They found the melting point of their compound to be 53°, while we find the melting point of our tribrompropionic acid to be 92°.

BUFFALO, N. Y., *Jan.* 5, 1880. NATICK, MASS.

ON A NEW SYNTHESIS OF SALIGENIN.

By WM. H. GREENE.

The method by which I have obtained saligenin synthetically is an application of a general method for the preparation of phenolic derivatives made known by Reimer and Tiemann. Indeed, since by the reaction of chloroform or of carbon tetrachloride on an alkaline solution of sodium phenate, salicylic aldehyde, or salicylic acid may be obtained, it may naturally be expected that, under the same circumstances, methylene chloride would yield saligenin, the latter being an oxybenzylic alcohol.

A mixture of 30 grams of methylene chloride, 30 grams of phenol, and 40 grams of sodium hydrate dissolved in 50 grams of water, was heated in a sealed matrass in a water-bath. The

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* Ann. der Chemie, 195, 73.

reaction is complete in about six hours, after which the contents of the matrass are neutralized with hydrochloric acid, and agitated with ether, which takes up the saligenin and the excess of phenol. The ethereal solution is decanted, and the ether distilled off; the residue is repeatedly exhausted with boiling water, which takes up the saligenin, and leaves the greater part of the phenol undissolved. The aqueous solution is concentrated to a small volume, and the drops of phenol which separate on cooling are removed. After exposing the residue for some time over sulphuric acid, a crystalline mass is obtained, which is pressed and recrystallized from boiling water or from alcohol. Pure saligenin is thus obtained.

The quantity of saligenin is by no means in proportion to the quantity of phenol employed, and an alcoholic solution of sodium hydrate yields no better results than an aqueous solution, although the reaction takes place more promptly.

Isomeric oxybenzylic alcohols may be, and probably are, found at the same time, but I have not yet been able to isolate such compounds.

ON THE DECOMPOSITION OF ALCOHOLS, ETC., BY ZINC CHLORIDE AT HIGH TEMPERATURES.

By J. A. Le Bel and Wm. H. Greene.

Wischnegradsky having demonstrated the presence of normal amylene (propyl-ethylene) in commercial amylene, prepared by the action of zinc chloride on ordinary amylic alcohol, we were led to determine whether normal butylene could not be produced by the decomposition of ordinary butylic alcohol by zinc chloride at high temperatures.

Our results induced us to extend the experiment to other alcohols, and the reactions observed, although extremely brutal, are interesting, as they indicate the more stable linkings of the carbon atoms.

The experiments were made in a manner similar to that employed by Etard in the preparation of amylene. The zinc chloride was strongly heated in a mercury bottle provided with two apertures, through one of which the alcohol was allowed to fall upon the fused zinc chloride in a thin stream, or in quick successive drops, while the other served for the passage of a rather wide delivery tube, so arranged that it could be cleared, if it became obstructed, without discontinuing the operation.

The products of the decomposition were passed through a condensing apparatus and receiver, for the collection of undecomposed alcohol and liquid matters, while the gases were led through bromine, for the absorption of unsaturated hydrocarbons. In some cases a bottle of ammoniacal cuprous chloride was introduced between the receiver and the bromine bulbs, for the retention of acetylene, if present, and the apparatus was otherwise modified to suit the body under experiment. The observations were directed especially to the hydrocarbons formed, and the other products were not examined, except in the cases mentioned.

Methyl Alcohol.

Since the general action of zinc chloride upon the other alcohols results in a dehydration, of which the simple or condensed olefines are the principal products, it was natural to expect that the decomposition of methyl alcohol under the same circumstances would yield analogous results. However, the reaction takes place in an entirely different manner: if the ordinary delivery tube be employed and directly connected with the condenser, the latter soon becomes obstructed by a solid product. A wide adapter was therefore introduced between the mercury bottle and the condenser, and a considerable quantity of a well-crystallized, not very fusible, solid substance sublimed on its sides.

The liquid products contained undecomposed alcohol, water, and a small quantity of non-saturated hydrocarbons, too numerous and in too small quantity for complete investigation.

The gases were washed by passage through sulphuric acid, and then conducted through bromine. The sulphuric acid absorbed a small quantity of methyl oxide, which was subsequently set free by diluting the acid with water. Only traces of gaseous olefines were absorbed by the bromine, the bromides obtained consisting of propylene and butylene bromides. The great mass of the gaseous products consisted of saturated hydrocarbons, of which methane was found to be the principal constituent.

The crystals condensed in the adapter were purified by repeated crystallization from alcohol; they obstinately retain a trace of oily matter, and apparently a volatile product containing chlorine, from which they cannot well be freed by sublimation. When quite pure they constitute shining white scales, which melt at 160°, and boil at 259–260°. Repeated analysis shows them to be hexamethylbenzol, which was discovered by Friedel and Crafts, by the reaction of methyl chloride on benzol in presence of aluminium chloride. By the courtesy of M. Friedel we were able to compare our product with the hexamethylbenzol obtained by him, and to establish a perfect identity in the crystalline form, and in the picric acid compounds of the substances.

It is not easy to explain the formation of hexamethylbenzol in this reaction. Lest it might be due to the presence of acetone or other impurity in the methyl alcohol employed, the experiment was repeated with absolutely pure methyl alcohol prepared from methyl formate, and kindly furnished us by MM. Bardy and Bordet, who discovered this method for its preparation.* The result was the same as in the first case.

The evolution of small quantities of hydrochloric acid in these reactions was demonstrated. The normal product of the dehydration of methyl alcohol would be CH_2, and it may be easily conceived that acetylene is formed at the same time, and immediately condensed into benzol. We may then consider it possible that methyl chloride may be formed in the presence of benzol and zinc chloride; but the latter acts, in such a case, like aluminium chloride, producing benzol substitution compounds, and the hexamethylbenzol may be formed in this manner. However, it is worthy of note that the most careful experiments failed to indicate the presence of acetylene in the gases evolved.

Ethyl Alcohol. (*Wm. H. Greene.*)

The uncondensed products of this decomposition were passed through petroleum, before entering the bromine bulbs, in order to absorb any butylene which might be formed by polymerisation. Between the mercury bottle and the condenser the vapors were caused to traverse a small bulb containing water, which was afterwards found to have absorbed a small quantity of hydrochloric acid. The unabsorbed gases consisted almost entirely of hydrogen with a trace of ethane.

The bromide obtained was found to be ethylene bromide, containing no higher products, and mere traces of absorbed gases were obtained from the petroleum.

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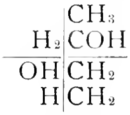
* Comptes rendus, 88, p. 183.

But while thus far the reaction was such as might have been expected, an examination of the condensed liquid showed that in addition to undecomposed alcohol, water, traces of ether, and a small quantity of liquid hydrocarbons, a considerable proportion of aldehyde had been formed. Subsequent experiments demonstrated that the proportion of aldehyde corresponded very closely with that of the ethylene disengaged, and the following equation probably expresses the decomposition:

$$2C_2H_6O = C_2H_4O + C_2H_4 + H_2O + H_2.$$

This may be understood from the following scheme:



$$\begin{array}{r|l} & CH_3 \\ H_2 & COH \\ \hline OH & CH_2 \\ H & CH_2 \end{array}$$

Some paraldehyde is also obtained, and is probably formed by the polymerisation of part of the aldehyde by the hydrochloric acid; the latter is due to the decomposition of the zinc chloride by the water generated, with the formation of oxychloride.

Propyl Alcohol. (*J. A. Le Bel.*)

The decomposition of propyl alcohol is analogous to that of ethyl alcohol; a somewhat larger quantity of oily matter is formed, and perhaps less propionic aldehyde. The chief interest attached to the results lies in the fact that the process is an advantageous one for the preparation of propylene. The unsaturated gaseous hydrocarbons consist almost wholly of that body, and large quantities of propylene bromide may be thus prepared in a short time from propyl alcohol.

Isobutyl Alcohol.

Inasmuch as there was a possibility of the formation of the three isomeric butylenes in this experiment, the gases disengaged were repeatedly washed by passing through sulphuric acid diluted with half its volume of water, in order to remove as much as possible the isobutylene. The absorbing apparatus which we found to answer best consisted of a number of wide, inclined tubes, about half filled with the acid mixture, through which the gas passed rapidly as it was formed. It was then led through bromine, and the bromides obtained were submitted to careful fractionation.

The liquid portion of the product seemed to contain butyl oxide, together with some ethers that were not examined.

About 1500 grams of isobutyl alcohol were employed, and nearly 1000 grams of mixed bromides obtained; the product was divided into three fractions: 145–152°, 152–154°, 154–160°. The latter fraction constituted about three-fifths of the entire quantity, and little or no residue remained at 160°, showing that ethylvinyl, of which the bromide boils at 166°, is not formed in the reaction. The bromide boiling between 154 and 160° consists of the bromide of normal dimethyl-ethylene, but it cannot be completely separated from the lower bromide (isobutylene) by fractional distillation.

The constitution of the bromide (154–160°) was verified by reconverting it into butylene by the action of sodium, again passing the gas through sulphuric acid diluted with half its volume of water, and then into concentrated hydriodic acid. The butyl iodide thus formed was decanted, dried and distilled, and was found to consist entirely of the secondary iodide, boiling at 118–119°: the tertiary iodide boils at 98°.

As we possessed a quantity of the bromide of ethylethylene, boiling at 166°, it was interesting to determine whether, as theory would indicate, the two normal butyl iodides would regenerate the same butylene, or whether the original hydrocarbon would be formed. If each of the hydrogen atoms united to the same carbon atom fill the same function, the hydriodates of normal dimethylethylene and of ethylethylene should be identical—should both be secondary butyl iodide; but if the hydrogen atom be still affected by the iodine atom with which it entered the group, it might be expected that the original hydrocarbon would be regenerated in each case on the removal of HI. The ethylethylene bromide was, therefore, heated with sodium, the resulting butylene was converted into butyl iodide as before, and the iodide was found to boil at 118–121°.

This iodide and that obtained by the preceding operation were separately decomposed by alcoholic potassium hydrate, and the butylenes produced were absorbed by bromine. In each case the bromide obtained was that of normal dimethylethylene, thus showing that the bromide of ethylethylene or ethylvinyl cannot be regenerated.

Normal Butyl Alcohol.

After the preceding experiment, it was interesting to ascertain, by the decomposition of normal butyl alcohol, whether the more stable position of the carbon chain be that of dimethylethylene or of ethylvinyl. The normal butyl alcohol used was prepared by the fermentation of glycerin by the process of A. Fitz, who furnished one of us with the butyl *bacillus*. The apparatus was arranged as in the preceding experiment, the gases being washed by passing through sulphuric acid, and then conducted into bromine. Immediately at the close of the operation the sulphuric acid was diluted with water at 0°, saturated with sodium hydrate, and distilled. Repeated and careful fractional distillation of the product failed to disclose the presence of trimethylcarbinol, showing that no isobutylene is formed in the decomposition.

Of 138 grams of bromides obtained, 87 grams distilled between 153 and 159°, and only 12 grams passed between 163 and 170°. Naturally, no bromide boiling between 145 and 150° was obtained. Therefore, besides the small quantity of ethylvinyl formed, the only gaseous olefine produced by the reaction consists of normal dimethylethylene, and in this case the normal carbon chain shows no tendency to transformation into a modification having side-chains.

A. Etard[*] studied the action of zinc chloride at high temperatures upon ordinary amylic alcohol, and considered the product boiling between 35 and 38°, as isopropylethylene, but Wischnegradsky[†] showed that Etard had obtained trimethylethylene, isopropylethylene boiling at 21.5°.

Aldehyde. (*Wm. H. Greene.*)

The aldehyde was allowed to flow in a thin stream upon the fused zinc chloride, for when dropped, the greater part of it volatilizes immediately on entering the hot mercury bottle.

The gas evolved was passed through ammoniacal cuprous chloride; no acetylenic precipitate was formed. Of the bromides obtained, the greater proportion consisted of ethylene bromide, while a considerable portion of propylene bromide, and a small quantity of higher bromides were obtained.

The condensable products of the decomposition consisted of water, unaltered aldehyde, crotonic aldehyde, and paraldehyde; the latter is attributable to the polymerising action of the hydrochloric acid set free, on the aldehyde which escaped decomposition, a noticeable evolution of hydrochloric acid having been observed in this experiment. As in the other cases, a small proportion of the distillate consisted of a complex mixture of hydrocarbons.

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[*] Comptes rendus, 86, 488.

[†] Ibid. 86, 973.

Acetone. (*Wm. H. Greene.*)

The disengagement of saturated hydrocarbons was comparatively insignificant, and the unsaturated hydrocarbons consisted principally of the higher members of the series; only a small quantity of ethylene bromide, and somewhat more propylene bromide, were obtained, the thermometer then rising rapidly during the fractionation, until it reached 250°, when the distillation was stopped.

It was to be expected that mesitylene would be formed in this reaction, but the quantity of oily distillate was quite small, and no mesitylene could be detected by the most careful examination. However, a considerable proportion of the oily matter which condensed was found to consist of hexamethylbenzol. In order to separate this, the aqueous portion of the distillate was removed, and the lighter layer was distilled until the residue consisted only of the little remaining water and an oily layer. The latter was decanted and again heated until hexamethylbenzol began to sublime; the residue was allowed to cool, strongly pressed, and the hexamethylbenzol was purified by sublimation and crystallization from hot alcohol.

The yield of hexamethylbenzol is very small, not nearly as large as that obtained from methyl alcohol.

Acetic Acid. (*Wm. H. Greene.*)

The gaseous products which escaped absorption by the bromine, consisted of carbon monoxide and carbon dioxide, together with a small quantity of saturated hydrocarbons.

The bromides formed contained a little ethylene bromide, mere traces of propylene bromide, and the bromide of dysymetric dimethylethylene (isobutylene) in considerable quantity. At the same time an appreciable amount of the bromide of normal dimethylethylene was obtained.

The formation of isobutylene in this reaction is quite unexpected, and not entirely intelligible, for a comparison of the relative quantities of the products shows the final results, carbon monoxide, carbon dioxide and butylene, to be in about equal molecular proportions.

ON THE DETERMINATION OF NITROGEN.[*]

BY S. W. JOHNSON AND E. H. JENKINS.

In the Station Report for 1878[†] the comparative merits of the two methods employed by chemists for the quantitative determination of nitrogen in agricultural products were discussed, and full details were given of the precautions which our experience has led us to adopt in applying the soda-lime process. The notion that the so-called "absolute method" is more exact than the soda-lime process, and that the albuminoid bodies can only be analyzed by the former method, made it necessary to submit both processes to critical experimental study, and our conclusion was that the two methods, when properly worked, give results that agree within 0.05 to 0.15 per cent. We found, moreover, confirmation of the long recognized fact that the errors of the soda-lime process naturally tend to give a deficiency, and those of the absolute method an excess of nitrogen. We give but a brief outline of our mode of working the absolute method. The circumstance that other chemists are still undecided as to the merits of the two processes, and that the absolute method must be frequently employed in the analyses of fertilizers containing both nitrates and organic nitrogen, decides us to give a detailed account of the procedure which we have adopted and which gives us so satisfactory results.

Reagents.

Cupric Oxide.—"Copper scale," which may contain cuprous oxide, coal dust, oil, etc., is mixed in an iron pot with 10 per cent. of potassium chlorate and enough water to make a thin paste. The mass is heated and stirred till dry, the heat is then raised to the point of ignition, and continued until the mass does not glow nor sparkle when stirred.

The potassium chloride is washed out by decantation and the cupric oxide is dried and moderately ignited.

Metallic Copper.—Granular copper oxide, or fine copper gauze, is suitable for its preparation. The granular copper is most con-

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[*] From the Report of the Connecticut Agricultural Experiment Station for 1879. Communicated by the Authors.

[†] Also this Journal, Vol. 1, p. 74.

venient; copper gauze must be made into rolls adapted to the combustion tube. The copper is reduced and cooled as usual in a stream of hydrogen.

Potassium Chlorate.—Commercial potassium chlorate is fused in porcelain and pulverized.

Sodium Bicarbonate must contain no organic matter.

Solution of Caustic Potash.—Dissolve commercial "stick potash" in less than its weight of water, making a solution so concentrated that, on cooling, it deposits crystals of potassium hydrate.

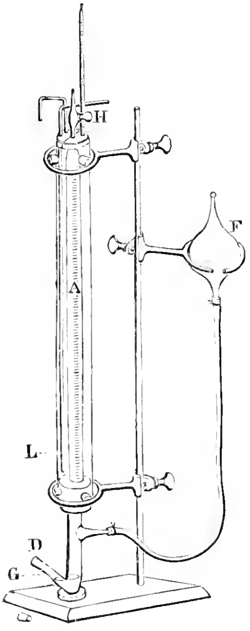
The same clear solution may be used for a number of combustions or until the absorption of carbonic acid gas is not quite prompt.

Apparatus.

The Combustion Tube should be of the best hard Bohemian glass, about 2 feet 4 inches long. The rear end is bent and sealed as in Fig. 3. It is best to protect the horizontal part with thin copper. The tube is connected with the pump by a close-fitting rubber cork, smeared with glycerine.

Azotometer.—This is a modification of the apparatus invented and described by Schiff, *Fres. Zeitschrift*, Bd. 7, p. 430. It is represented in Fig. 1. The gas is measured in an accurately calibrated cylinder (burette), A, of 120 c. c. capacity, graduated to fifths of cubic centimeters, and closed at the upper end by a glass stopcock. The lower end is connected by means of a perforated rubber stopper about 1¾ inches long and 1½ inches diameter, with another tube having two arms, one, D, to receive the delivery tube from the pump, the other connected by a rubber tube with a bulb of 200 c. c. capacity, F, through which potash solution is supplied. The graduated tube is enclosed in a water-jacket with an external diameter of about 1¾ inches. Its lower end is closed by the caoutchouc stopper that connects the two parts of the azotometer described above. The upper end of the jacket is closed by a thin rubber disk slit radially

Fig. 1.

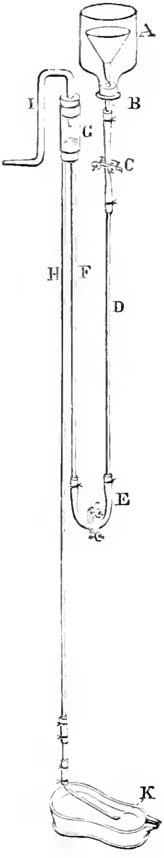


and having four perforations: one in the centre, through which the neck of the graduated tube passes, and three others near the circumference. Through one of the latter, a glass tube, L, bent as in the figure, reaches to the bottom of the jacket, another short tube passes through the disk and the third hole is for supporting a thermometer. The azotometer is held upright and firm on a string by rings fitted around the jacket and by cork wedges.

The bulb for potash solution rests in a slotted, sliding ring.

The air pump used is the Sprengel mercury pump, modified merely so as to be easily constructed and durable. Its essential parts are sketched in Fig. 2. Some of them are exaggerated in order to show their construction more plainly. Through a rubber stopper wired into the nozzle of the mercury reservoir, A, passes a glass tube, B, 4 inches long, this connects by a caoutchouc tube with the straight tube, D, 3 feet long. The rubber tube, E, 6 inches long, connects D with a straight glass tube, F, of about the same length as D.

Fig. 2.



G is a piece of combustion tube 1½ inches long, closed below by a doubly perforated soft rubber stopper admitting the tubes F and H, and above by a singly perforated rubber stopper into which a tube, I, is fitted. The tube H has a length of 45 inches. At the bottom it is connected by rubber with a straight tube of 3 inches, and this again with a tube, K, of 7 inches. The tubes H K should have an internal diameter of 1½ millimeters, F may be 2 millimeters, and D still larger.

We have used for H and F slender Bohemian glass tubes of 4 millimeters exterior diameter. Their elasticity compensates for their slenderness. If heavy barometer tubes be used the stoppers and G must be of correspondingly larger dimensions.

The joints at G must be made with the greatest care.

It is best to insert the lower stopper for half its length into G, having the dimensions of the parts so related that it requires considerable effort to force the slightly greased tubes F and H to their places just through the stopper. The tube I must be of *stout glass* — a decimeter in diameter. It is drawn out at either end to a long taper, and bent as in the figure, in order to bring its free extremity to the level of the combustion furnace. The hole in the upper rubber stopper has a diameter of 5 mm., just sufficient to admit the narrowed end of the tube, which, after greasing or moistening with glycerine, is "screwed down" into the stopper.

These three joints are the only ones belonging to the pump which have to resist diminished pressure, and require extreme care in making.

If not entirely secure they are to be trapped with glycerine. For this purpose it is needful to pass F and H through a stopper of half an inch greater diameter than G and correspondingly perforated, before entering the latter. Then, previous to inserting I, a tube 4 inches long is slipped over G upon this wider stopper. When I has been inserted and the tubes have been secured to their support, the space between G and the outer tube is filled with the most concentrated glycerine, which is prevented from absorbing moisture by corking above.

The two rubber tubes are both provided with stout screw clamps, to admit of exactly regulating the flow of mercury. The tubes D, F, H, and I are secured to a vertical plank framed below into a heavy horizontal wooden foot on which rests the mercury trough, and having above a horizontal shelf through an aperture of which passes the neck of A.

The tubes D, F, H, and I are secured to the plank at several points by wooden or cork clamps, clasping the tubes and fastened by screws or wires.

These fastenings are made elastic by the intervention of a thick rubber tube between the glass and wood. The connections C and E should be made of stout vulcanized rubber, those at the base of H K of fine black rubber.

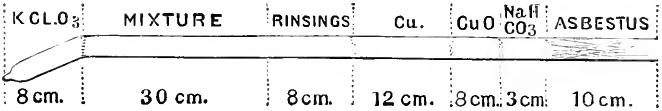
The latter should be soaked in melted tallow previous to use, all excess being carefully removed from the interior. The joints should be wound with waxed silk.

A glass funnel is placed within A to prevent spattering of the mercury when it is filled.

Operation.

From 3 to 4 grs. of potassium chlorate, according to the amount of carbon to be burned, are put into the tail of the combustion tube, Fig. 3, followed by an asbestos plug just at the bend.

Fig. 3.



The substance to be analyzed (0.6–0.8 grams) is well mixed in a mortar with enough cupric oxide that has been *freshly ignited* and allowed to cool, to make a layer 11 or 12 inches long in the tube. The mixture is introduced through a funnel and rinsed with enough cupric oxide to make a layer of 3 inches, a second asbestos plug, and upon it a layer of reduced copper of 4 or 5 inches long are put in, then a third asbestos plug, then 2 inches of cupric oxide, a fourth asbestos plug, then .8 to 1. grams of sodium bicarbonate. The remaining space in the tube is loosely filled with asbestos, to absorb the water which is formed during combustion, and prevent it from flowing back upon the heated glass. The anterior part of the tube containing the cupric oxide and reduced copper is wound with copper foil, leaving, however, a little of the copper (Cu. in fig. 3) visible at its rear. The combustion tube is placed in the furnace at the level of the tube I, and connected with the latter by a close-fitting rubber stopper smeared with glycerine.

Care must be taken to make the joint perfectly tight. The combustion tube has its conical rubber stopper partly inserted, and is then forced and rotated upon the tapering and stout end of the tube I, the latter being supported by one hand applied at the lower bend.

Preparation of the Azotometer.

Fill the bottom of the azotometer to about the level indicated by the dotted line G, with mercury. Close the arm D securely with a rubber stopper. Grease the stopcock H and insert the plug, leaving the cock open.

Pour potash solution into F till A is nearly full, and there is still some solution in the bulb F. Raise the bulb cautiously with one hand, holding the stopcock H in the other hand. When the solution in A has risen *very nearly* to the glass cock, close the latter, avoiding contact of the alkali with the ground glass bearings. Replace the bulb in the ring and lower it as far as may be. If the level of the solution in the azotometer does not fall in 15 or 20 minutes, it is tight. Place the delivery tube of the pump K in a mercury trough.

Supply the vessel A with at least 500 c. c. of mercury. Cautiously open the clamps C and E. If the mercury does not start at once pinch the rubber at E repeatedly. The mercury should flow nearly as fast as it can be discharged at K, without filling the cylinder G. Five to ten minutes working of the pump will generally suffice to make a complete exhaustion of the combustion tube. If most of the mercury runs out before exhaustion is complete, close the clamp C, return the mercury to A, and repeat the operation. When there is a complete exhaustion, the mercury falls with a rattling or clinking sound. After it has been distinctly heard for half a minute, close the clamp C. If the mercury column in H remains stationary for some minutes, the connections are proved to be tight.

Adjusting the Azotometer.

Remove the mercury trough, placing the K in a capsule.

Heat the part of the tube containing sodium bicarbonate. Water vapor and carbon dioxide are evolved, which fill the vacuum in H and expel the mercury. While this is being done place the azotometer near by, remove the bulb F from the ring and support it in a box near the level of D, so that the stopper may be removed from D without greatly changing the level of the mercury G, and so that the azotometer can be moved freely without disturbing it. When the cork in D has been removed fill D half full or more with water.

As soon as the mercury has fully escaped from K insert the latter in D. Let a few bubbles escape through the water, and then pass the tube K down so that the escaping gas enters the azotometer. It will much facilitate the delivery of gas if the extremity of the tube K just touches the inside of the azotometer tube, and is kept, as near as possible, to the surface of the mercury.

The carbon dioxide is absorbed in passing through the caustic potash solution. In spite of all precautions very minute bubbles of permanent gas will occasionally ascend, but, as will be seen on observing the amount of potash solution thus displaced, the error thereby occasioned is extremely small.

The Combustion.

First heat the anterior cupric oxide to full redness, and afterwards the copper. The fine gauze or pulverulent copper very completely reduces any oxides of nitrogen which might be produced in the combustion, and also retains any excess of oxygen which is evolved at the close of the process.

The anterior cupric oxide burns the traces of hydrogen which may be held by the reduced copper, even when the tube is exhausted, and also destroys the carbon monoxide which is usually formed when steam and carbon dioxide pass together over reduced copper, if iron or carbon be present. Go on with the combustion as usual, bringing the heat up to a fair redness. The flow of gas may be made quite rapid, say one bubble a second, or a little faster.

When the horizontal part of the tube has all been heated, and the evolution of gas has nearly ceased, heat the potassium chlorate so that it boils vigorously from evolution of oxygen. The reoxidization of the reduced copper oxide and of any unburned carbon proceeds rapidly.

When the oxygen, whose flow admits of easy regulation, begins to attack the anterior layer of reduced copper, stop its evolution and lower the flames all along the tube, keeping the reduced copper still faint red.

After a few minutes start the pump, slowly at first, having some vessel under the tube D of the azotometer to receive the mercury. A few minutes pumping suffices to clear the tube. Remove the azotometer, close the tube D with its rubber stopper, then raise the bulb into its ring to such a height that the potash solution in it shall be at about the same level as that in the graduated tube. Connect L at its upper end with a water supply, insert a thermometer in the top of the water-jacket and let the water run until the temperature and the volume of gas are constant.

Read off the volume of gas and the temperature, after having accurately adjusted the level of the solution in the bulb to that in the azotometer.

Read the barometer and make the calculations in the usual way. When 50 per cent. potash solution is used, no correction need be made for tension of aqueous vapor, as Schiff has shown.

The calculation is somewhat shortened by the use of the table in *Jour. of Chem. Soc.* Vol. 18 (1865), p. 212.

Very fair results are got by employing, with suitable precaution, a stream of carbon dioxide to displace the air of the combustion tube, but the process is very tedious, the sources of error are more numerous, and the results are apt to be higher and not so accordant as when the mercury pump is used to evacuate the tube.

The pump above described has been in use for eighteen months without any repairs, and by its help two or even three analyses may be performed in a day.

The paper in Station Report for 1878, already referred to, gives results of analyses of a variety of substances by the method above described.

Some additional comparative analyses recently made by Dr. Jenkins, on carefully prepared, but not dry, albuminoids have given the subjoined results for nitrogen:

	By Soda Lime.	By Absolute Method.	Average Differences.
Albuminoid of Pea Nuts, - -	15.95	15.92	——
Legumin of Peas, - - -	15.32–15.27	15.41	0.11
Conglutin of Almonds, - - -	16.32–16.37	16.59	0.25

GUM LAC FROM ARIZONA.

By J. M. Stillman.

There was received lately at this University, sent by Mr. John A. Culbertson, of Phœnix, Arizona, a quantity of a substance of resinous character, forming a coating of considerable thickness on the twigs of a plant called in that neighborhood "Greasewood," but which I am assured by Prof. Hilgard and by Dr. A. Kellogg is the *Larrea Mexicana.* The plant was identified by means of leaf, flower and seed sent by Mr. Culbertson. The specimens were gathered in the vicinity of that place on the 22d of December last.

The form of occurrence is precisely the same as that in which the gum lac of India is said to occur, as a coating of hard, brittle resin of a reddish color. The gum lac from Siam is said to occur sometimes in deposits of a quarter of an inch in thickness. None of these specimens are so thick, but some exceed ⅛ inch in thickness, and most are of nearly that thickness.

The gum lac of India is of cellular structure, and in these cells are developed the ova of the insect (*Coccus lacca* or *C. ficus*) whose puncture is said to cause the exudation. These cellular cavities contain at the proper season a red substance, which probably serves as the food of the young insects and in which the eggs are deposited.

The specimens from Arizona exhibit the same structure, and in working with the gum the fingers were frequently stained by the crushing of the pulpy substance of blood-red color, in which the eggs could be readily perceived with the lens or microscope.

The following characteristic properties of the gum lac, given by various authors, have been found to be also properties of the specimens examined by me.

(1) Contains a red coloring matter, partly soluble in water (and resembling cochineal). I found 3 per cent. of such coloring matter by one method, 1.4 per cent. by another method given below. (2) Partly soluble in alcohol with a reddish color. (3) Almost entirely soluble in dilute caustic alkalies with a deep red color. (4) The resin of the gum lac (shell lac) is soluble in dilute borax solutions on heating with a purplish red color, and the solution has a peculiar sweetish odor. The resin of this product also is soluble in dilute borax solution, the color is a little brighter red and the odor a little stronger than in the case of the shell lac, but this may be owing to the greater freshness of the Arizona product, as the shell lac used for comparison was at least four or five years old. (5) The lac resin softens at comparatively low temperatures. This product becomes soft and plastic when it feels but just warm to the touch. (6) When warm has a peculiar aromatic odor.

Quantitative analyses of the crude lac (stick lac) have been made by different chemists with varying results.

HATCHETT.	
Resin	68.0
Wax	6.0
Coloring matter	10.0
Gluten	5.5
Foreign bodies ..	6.5
Loss	4.0

DR. JOHN.	
Resin sol. in ether	66.65
" insol. "	16.75
Coloring matter ..	3.75
Extractive ..	3.92
Insect skins ..	2.08
Wax	1.67
Laccic acid ..	0.62
Salts	1.04
Sand	0.62
Loss	2.90

FRANKE.	
Resin ..	65.7
Substance of the lac	28.3
Coloring matter	0.6
	94.6

It will be seen from these that *exact* analysis of the lac into its various constituents could not identify it with the India lac when no two analyses agree on the constituents nor on the proportions, the resins being given at from 65.7 to 83.40, and coloring matter at from 0.6 to 10.0 per cent. A partial analysis, however, was made for the purpose of establishing identity as far as could be done by this means.

A portion of the Arizona stick lac was carefully removed from the twigs and boiled with water, and in this way 3.0 per cent. of deep red coloring matter (colored extract) was obtained. The residue was extracted with boiling alcohol, and about 61.7 per cent. of alcoholic extract, probably mostly resin. Of the residue the greater portion was soluble in dilute caustic potash with deep red color, and reprecipitated by acetic acid for the most part, though a certain coloring substance soluble in caustic potash, but not precipitated by acetic acid, could be detected by again neutralizing the acid filtrate.

A second more thorough examination was made by first extracting the powdered resin, dried before weighing, with hot absolute alcohol, which was found to leave the coloring matter nearly all behind; then extracting the residue with boiling water, and extracting the residue from this with dilute caustic potash. The final insoluble residue was dried and weighed, the alcoholic extract and deep red aqueous extract both evaporated, dried and weighed, and caustic potash solution precipitated with acetic acid, filtered, washed on the filter, and the precipitate dried and weighed. By this process there was lost a certain amount of coloring matter insoluble in water but soluble in caustic potash, but not precipitated by acetic acid, but easily detected in the filtrate and wash-water.

The results of these determinations gave—

Resins, &c., soluble in absolute alcohol. . .	61.7
Coloring matter, (soluble in water) . . .	1.4
Caustic potash extract, ("lac stuff"?) . . .	26.3
Insoluble residue, ...	6.0
Loss, (including some coloring matter) . .	4.6
	100.0

The 26.3 per cent. seems to correspond to what Franke calls "material of the lac" (Muspratt), of which he finds 28.3 per cent. in India stick lac.

It will be seen then how closely the gum lac from Arizona agrees in characteristic properties, structure and chemical composition with the India varieties. The differences in the analyses quoted are due doubtless partly to different methods of analysis, partly to real differences in different specimens (this is probably peculiarly applicable to the coloring matter), and partly to different interpretations of the results of analysis.

I am informed by Mr. Culbertson that the insect and gum are also found on a thorny bush called "cat-claw" by the residents. It would be very interesting to have the insect identified or compared with the Indian coccus, as their mode of life as well as the products of their activity appear identical.

Since writing the above communication I have received from Arizona specimens of the lac coating the twigs of that plant which is identified by Professor Hilgard, of this University, as the *Acacia greggii.*

The lac from this source agrees in its main chemical properties with that from the Larrea, behaves the same towards the reagents mentioned in the previous description. It resembles it also in general appearance and in its irregular cellular structure.

It is however much scantier on the twigs of the Acacia, and the amount of coloring matter is notably less. This is shown by the color of the caustic potash solution, and of the borax solution being much lighter red than the solutions of the lac from the Larrea, and also by the fact that the specimens of Acacia lac examined gave no red coloration to water by boiling. It was noticed, however, that when alkalies were added to this water, the color became a bright red. A quite appreciable quantity of alkali was needed before this action took place, pointing to the existence of an acid in the lac which had first to be neutralized before the color could be reddened—possibly Dr. John's *laccic acid* (Muspratt's Chemistry). It is quite possible that this difference in contents in coloring matter is simply due to the fact that the two specimens represented different stages of development. The twigs of the Acacia were dry, and the leaves fallen when these specimens were collected. No fresh insect eggs with the purple juice, with which they are covered, could be detected in the cells of these specimens, while in the specimens from the Larrea this was frequently observed, and moreover the Larrea was in leaf and flower when the specimens were collected. It is quite possible that at other times this difference in the amount of dye-stuff may not exist.

From observations by a number of gentlemen acquainted with that portion of the country, it appears that the Larrea lac is very widely distributed throughout Arizona and the southern part of California (Mohavo and Colorado deserts), and the gum is used by the inhabitants in place of solder for mending kettles, etc. This use is suggestive of the use of the India lac for the manufacture of sealing-wax. Experience must show whether these products are of such quality as to eventually prove of commercial value.

UNIVERSITY OF CALIFORNIA, *March* 11, 1880.

ETHEREAL OIL OF CALIFORNIA BAY TREE.

BY J. M. STILLMAN.

The California bay tree, known under the different botanical names of *Oreodaphne Californica*, *Laurus Californica*, *Tetranthera*, and latterly *Umbellaria Californica*, is a large and beautiful evergreen tree, very common to the valleys and water-courses of the coast mountains of California. It often attains great size, and its timber is much used under the name of "California laurel" for veneering and fine cabinet-work. The leaf is in shape something like the laurel, but lighter in color and narrower. Both leaf and wood have a very fragrant aromatic odor, which when strong, as in the crushed leaf, excites the mucous surfaces, brings tears to the eyes and produces headache.

The oil was obtained by distilling the leaves (which were gathered in March 1879 when the trees were in bloom) with steam. In the neighborhood of sixty or seventy pounds of the fresh leaves were placed in a large barrel with perforated false bottom, and steam from the escape-pipe of a steam-boiler forced through the mass and condensed. In order to avoid the accumulation of too large an amount of water, this was siphoned off from the bottom of the receiving bottle, the siphon dipping into a dish of water by the side of the bottle, and the overflow of this dish kept the water in the bottle at a constant level. At the end of two days there were obtained in this way 820 grams of the oil. The oil as thus obtained is of a clear yellowish or straw color, of the peculiar aromatic odor of the leaf, specific gravity at 11° C. 0.94. By long standing (nearly a year) it does not thicken.

Subjected to fractional distillation it gives up a small quantity of dissolved water, and separates into two principal fractions, one boiling from 170–190° C. and the other from 210–225°, with smaller quantities passing over as high as 260°.

The lower fraction mentioned was subjected to repeated fractional distillation, and gave a considerable quantity of a clear, colorless, mobile liquid boiling at 167–168°, though apparently with slight dissociation, as traces of water appeared in the first portions of the distillate at each distillation, which were not to be got rid off by repeated distillation and removing the first portions of each distillate. A portion of the purest of this substance from 167–168° C. was subjected to elementary analysis.

		I.	II.	Mean.	Calculated for $C_{20}H_{32}.H_2O$.
C	...	82.91	82.46	82.68	82.76
H	...	11.93	11.68	11.80	11.72

It will be seen that the agreement is very close with the composition of a hydrate of turpentine in which one molecule of water is combined with two of $C_{10}H_{16}$ or one of $C_{20}H_{32}$.

This agrees with the terpinol of Wiggers, investigated and named by List, and obtained in various ways from the turpentine dihydrate $C_{10}H_{16}.2H_2O$. The boiling point of terpinol is given at 168°, and it is a colorless liquid of pleasant aromatic odor. The odor of the compound analyzed is not unlike that of spirits of camphor, though not quite identical.

It is not readily affected by metallic sodium, even when heated with it. The water is therefore in intimate combination, possibly as an ether $(C_{10}H_{17})_2O$.

A vapor density determination was made by Mr. J. B. Wilcutt according to Victor Meyer's method, in diphenylamine vapor. The result in one case gave 4.7, whereas the vapor density calculated for $C_{20}H_{34}O$ would give 10.0. If, however, dissociation should take place, splitting up the molecule into $C_{20}H_{32} + H_2O$, the vapor density of the mixture would be 5.0, not so far from the result obtained. That dissociation would take place was to be foreseen from the behavior on distillation, and was confirmed by the fact that after the operation the contents of the apparatus no longer had the original camphor-like odor, but possessed a distinct, rank odor of turpentine. It was also noticed that the compound itself by long standing bleached the cork of the test-tube, probably due to traces of the free $C_{20}H_{32}$ resulting from the distillation.

An analysis was made of a fraction boiling at 171–172°, which gave C=81.39; H=11.40. Evidently therefore a mixture of the above with the more oxygenated, higher-boiling constituent, umbellol, $C_8H_{12}O$.

The higher fraction (210–225°) was also subjected to fractional distillation and a compound obtained in considerable quantity boiling without decomposition at 215–216° (uncorrected). This substance is also a colorless mobile liquid of aromatic but powerful odor which, too strongly inhaled, attacks the mucous surfaces and causes headache. It is but slightly volatile, a quantity in an open watch-glass losing one mg. in an hour and a half. With concentrated sulphuric acid it gives a blood-red color, turning to brown and black. Water separates it from its solution in the acid. It is acted on violently by sodium, forming a blood-red, brittle, resinous substance; it is also acted on violently and decomposed by strong nitric acid. Elementary analysis gave

		I.	II.	III.	Calculated for $C_8H_{12}O$.
C	...	77.28	77.27	77.17	77.42
H	...	9.74	9.53	9.57	9.67

The vapor density determined, with the assistance of Mr. F. Slate, according to Victor Meyer, in diphenylamine vapor gave 4.39; calculated for $C_8H_{12}O$ = 4.29. The formula is therefore $C_8H_{12}O$.

It is isomeric, as far as I know, with no other known compound. It is homologous as far as its empirical formula is concerned with common camphor, but has different properties.

Analysis III. above was made two or three months later than the other two, after the substance had been standing in a test-tube corked, with occasional removal of the cork. It will be noticed that oxidation is very slow if it takes place at all, though a faint tint of yellow seemed to indicate such action. Experiments have been commenced with the object of determining the nature of these substances and their chemical constitution if possible, and I intend to subject the reactions and derivatives of these interesting compounds to an extended investigation. As other duties, however, entirely occupy me at present, I have been compelled to postpone further investigation on this subject for some months. I therefore make this preliminary report and take the opportunity to reserve the ground for future work.

UNIV. OF CALIFORNIA, *Feb.* 1880.

THE ELECTROLYTIC METHOD AS APPLIED TO CADMIUM.

By Edgar F. Smith.

Electrolytic Estimation of Cadmium.

During the past few months I have made additional experiments upon the electrolytic estimation of cadmium, and as they perhaps may be of some interest, I give them here.

1. 0.1209 gram cadmium oxide was dissolved in dilute hydrochloric acid, and to this solution an excess of pure sodium acetate added. I diluted with water to 25 c. c., and then connected the platinum crucible containing the mixture with the zinc pole of a two-celled bichromate battery. At the end of three hours the metal was completely precipitated in a regular, crystalline mass on the crucible sides. After washing with water, alcohol and ether, the crucible was dried and weighed. The cadmium found was 0.1049 gram; the CdO taken requires 0.1057 gram Cd.

2. 0.1087 gram CdO treated as above yielded 0.0950 gram Cd. Required Cd = 0.0951 gram. Time necessary for precipitation about the same as in 1.

3. In this experiment 0.1003 gram cadmium oxide was dissolved in an excess of nitric acid, and to this were added 3 c. c. of concentrated sodium acetate solution, and the whole then diluted to 25 c. c. with distilled water. In four hours the precipitation was complete. The deposit was not, however, as light colored as in case of the chloride. The salt can nevertheless be used, and where cadmium has been precipitated as sulphide it is only necessary to dissolve the same in as little acid as possible and add an excess of sodium acetate solution. The amount of cadmium found in the above example was 0.0877 gram, while the required amount was 0.0880 gram.

4. Dissolving 0.0832 gram cadmium oxide in dilute sulphuric acid I added as in previous experiments an excess of an alkaline acetate, and allowed the electric current to act upon the diluted solution for several hours. The deposition of the metal was rapid and in a beautiful, regular form. The oxide taken required 0.0728 gram metal, and I obtained 0.0725 gram.

5. Treating 0.1098 gram CdO as just mentioned, I found 0.0955 gram Cd instead of 0.0960 gram.

6. Again 0.1039 gram CdO yielded 0.0907 gram Cd instead of 0.0909 gram.

The appearance of the cadmium and the rapidity with which it separated from a sulphate solution containing an alkaline acetate led me to experiment with a pure sulphate solution. According to Wrightson,* this salt is little adapted to the electrolytic estimation of cadmium. My results, however, indicate just the opposite. In my first experiment I used a neutral sulphate solution.

1. 0.1110 gram CdO in form of sulphate was dissolved in 25 c. c. water and the usual battery connection adjusted. In two hours I obtained 0.0968 gram Cd instead of 0.0971 gram. Deposit regular and crystalline.

The next thing to be ascertained was whether the presence of free sulphuric acid was disadvantageous or not.

2. 0.1085 gram CdO was dissolved in sulphuric acid. 2 c. c. free H_2SO_4 (1.095 sp. gr.) were present. Diluted with water to 25 c. c., and in two hours the precipitation of the metal was finished. Found 0.0931 gram Cd instead of 0.0949 gram.

3. 0.1502 gram CdO in form of sulphate, with 2 c. c. H_2SO_4 (1.095 sp. gr.), and diluted with water to 27 c. c., yielded in three hours 0.1327 gram Cd instead of 0.1314 gram.

4. 0.1125 gram CdO as sulphate, having the same amount of free acid present, and being diluted to 25 c. c., gave in two hours 0.0986 gram Cd. Required Cd = 0.0984 gram.

5. 0.0897 gram CdO yielded 0.0863 gram metallic cadmium instead of 0.0860 gram.

The slight increase noticed in these examples is due to impurities in the salt employed. I prefer the sulphate to any other salt for the electrolytic estimation of this metal. When larger quantities of substance are taken than above given, it is advisable to place the cadmium solution in a beaker-glass and in this to suspend a crucible, upon which the deposit of metal may occur.

Separation of Copper from Cadmium.

In solutions of cadmium containing free nitric acid the electric current does not throw down the metal. Copper under the same conditions, however, is precipitated, providing too large an excess

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* Zeitschrift anal. Chemie, 15, 303.

of acid is avoided. In accordance with these facts I made several experiments with a view of separating the metals in this manner. These and their results are as follows:

Taking a mixture composed of 0.2220 gram copper sulphate and 0.0762 gram cadmium oxide in a little dilute nitric acid, I added to the same 2.5 c. c. concentrated nitric acid, then diluted the same with distilled water to 75 c. c. In this solution, contained in a beaker, I suspended a weighed platinum crucible connected with the zinc pole of a two-celled bichromate battery. A platinum wire dipping into the solution was attached to the opposite pole. In the course of six hours I carefully removed the crucible, upon which there was a fine copper coating, from the solution, taking care, however, not to interrupt the current until the vessel was entirely out of the acid liquid. The copper deposit was washed with water and alcohol, then dried and weighed. The amount of copper found was 0.0562 gram, the calculated 0.0564 gram. The deposit was dissolved and examined for cadmium, but none found. Nor was there any copper remaining in the cadmium solution. The amount of cadmium was not estimated in this instance, as some of the solution was lost by accident.

In a second experiment I took 0.3435 gram copper sulphate and .0911 gram CdO. These were dissolved in 100 c. c. water containing 3 c. c. concentrated nitric acid. The same battery power as already mentioned was employed. Allowing the current to act during the night, I obtained on the following morning 0.0874 gram Cu instead of 0.0873 gram calculated. This proved to be perfectly free from cadmium. The liquid containing the cadmium solution was evaporated to 50 c. c., potassium hydrate added in excess, and then a potassium cyanide solution sufficient to redissolve the precipitated cadmium hydrate. The crucible was again suspended in the liquid, and in five hours the cadmium was precipitated in fine, regular form. Four bichromate cells were employed. The found cadmium equalled 0.0789 gram instead of 0.0797 gram calculated.

Again in a third experiment I took 0.3070 gram copper sulphate and 0.0787 gram cadmium oxide. The solution was of the same dilution as before, containing also the same quantity of free acid. The deposited copper weighed 0.0779 gram and the calculated 0.0780 gram. No cadmium was detected in it. The cadmium thrown out by the current from a cyanide solution was 0.0690 gram instead of 0.0688 gram. Copper was not discovered in the cadmium solution. Instead of employing a cyanide solution for the precipitation of the cadmium, the nitric acid solution can be evaporated with sulphuric acid after the removal of the copper. The results with a sulphate solution are just as accurate.

LABORATORY OF THE UNIV. OF PA., *March* 15, 1880.

GALLIUM IN AMERICAN BLENDES.

BY H. B. CORNWALL.

Having observed the spectrum of the principal line of gallium, wave-length 417, I treated two European blendes and several American ones as follows. About one gram of each was treated with aqua regia, the solutions saturated with hydrosulphuric acid, filtered, evaporated to dryness, the residues redissolved in water containing a little hydrochloric acid, and the solutions treated with sodium carbonate until a slight precipitate formed. According to Lecoq de Boisbaudran these precipitates contained the greater part of the gallium which might be present. Each precipitate was dissolved in hydrochloric acid, evaporated nearly to dryness, redissolved in a few drops of water and observed with a single prism spectroscope and an induction spark from a coil capable of giving a five centimeter spark, but worked with a battery developing only about two-fifths of the power of the coil. Separate electrodes and glass tubes were used for each blende.

One European blende, from Pierrefitte, of medium richness according to de Boisbaudran, showed scarcely a trace of the gallium line; the other European specimen, from Santander, classed among the richest in gallium, showed it distinctly. The compact, greyish blende from Friedensville, Pa., showed it about as plainly, while a crystallized, rather dark, yellowish-brown specimen from Phœnixville, Pa., showed it more distinctly still. Two measurements of its position were made with a cross-hair eye-piece and vernier scale. They gave 416.92 and 417.05, mean 416.98.

To test the comparative richness of these blendes, two grams of each were treated with aqua regia, the solutions saturated with hydrosulphuric acid, filtered, evaporated to dryness, redissolved in water containing a little hydrochloric acid, and each solution diluted to five cubic centimeters. The Phœnixville blende showed the gallium line distinctly enough for approximate measurement. Two determinations gave 417.20 and 417.28. None of the other blendes responded to this test.

Finally, the gallium line was seen in a solution of about one gram of the Phœnixville blende, which had been prepared simply by treatment with aqua regia, filtration from undissolved sulphur, and concentration to a few drops.

The following minerals were also examined by the first method detailed above, viz.: zinc blende from Joplin, Mo.; Ellenville, N. Y.; Roxbury, Conn.; Warren, N. H.; Mine Hill, N. J.; calamine from Friedensville, Pa., and Sterling, N. J.; willemite, zincite and franklinite, from Franklin, N. J.

There is reason to believe that gallium occurs in the blendes from Joplin, Warren and Ellenville, since its line was seen more or less distinctly in case of each, and although the same electrodes were here used for all which had been previously used with a slightly stronger gallium solution, yet they were boiled with hydrochloric acid before each observation. Moreover, no gallium was detected in the case of the other three blendes and all of the oxidized minerals, the observations on which were irregularly interspersed among the others. Gallium may occur among blendes as rubidium does with the alkalies, widely spread in very small quantities.

Examination of other American zinc ores and products is still in progress, according to the simple and severe test applied to the Phœnixville blende, to ascertain whether any richer source of gallium exists here.

JOHN C. GREEN SCHOOL OF SCIENCE, PRINCETON COLL., *March* 5, 1880.

NITRIFICATION IN STANDARD AMMONIUM CHLORIDE SOLUTIONS.

BY H. B. CORNWALL.

The experiments of Warrington* on nitrification induced in dilute ammonium chloride solutions, containing acid phosphate of potas-

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* Chem. News, Dec. 14, 1877.

sium and seeded with surface soil, led him to the conclusion that darkness was apparently essential to the operation.

In the *Am. Jour. Sci.*, June, 1878, Storer gives several results which seem to support this view, so that Leeds* was induced to examine a standard solution of ammonium chloride, and stated that his experiments "confirm these results, so far as the change of the ammonium solutions in the dark is concerned, and give the rate at which it may be expected to occur under ordinary circumstances."

As long ago, however, as Nov. 26, 1877, Schloesing and Müntz† had stated that, in certain of their experiments, nitrification went on as well in the light as in the dark; a result similar to that obtained by E. W. Davy.‡

As I had been constantly making up my dilute ammonium chloride solution, for the "ammonia process" in water analysis, from a stronger standard solution of 3.15 grs. fibrous, commercial ammonium chloride in 1 litre of water, which had already stood nearly the whole of four years in a dark place, it became an object to ascertain whether any important change had taken place in it. Accordingly, in April, 1879, I made three determinations of the ammonia, precipitating as ammonio-platinic chloride and weighing the platinum after ignition, using 100 c. c. for one determination and 50 c. c. for each of the others.

Leeds had found that his standard solution. made with 0.7867 gr. of ammonium chloride to the litre, yielded only 0.00023 gr. of ammonia per cubic centimeter, instead of the 0.00025 which it should have given. Reduced to figures directly comparable I found in my three determinations 0.0002461, 0.0002461 and 0.0002465 grs. This solution therefore had lost less than one-sixtieth of its ammonia, instead of nearly one-twelfth, which Leeds found in a solution but one year old, and was consequently not practically injured for use in the water analysis.

The strength of my solution may have had some influence, but Storer's solution was equally strong, yet he reports a strong reaction for nitrites after about a year. As Leeds states that his solution showed a filamentous, apparently vegetable growth, while mine showed only a slight scaly deposit, probably from the glass of the bottle, it may be that the changes in some cases are due to the accidental introduction of germs from the atmosphere.

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* Proceed. Am. Chem. Soc. Vol. 2, Dec. 5, 1878.

† Comptes rendus, 85, 22.

‡ Chem. News, Dec. 3, 1879.

LABORATORY NOTES.

By Wm. L. Dudley.

On a Modification of Böttger's Test for Sugar.

The importance of an expeditious and reliable test for sugar is well understood, and in many cases where the presence or absence of sugar is of vital importance it is well to employ several tests in order to verify the results; and with this end in view I have been conducting some experiments with the bismuth test.

Böttger's test, which employs subnitrate of bismuth and sodium carbonate or sodium hydrate, is a good one; but the subnitrate is liable to contain silver, which on exposure to the light will give it a gray color. Also other impurities, having a tendency to render the results more or less unreliable, are often present.

After considerable experimenting the following modification was found to be very reliable: Dissolve subnitrate of bismuth in the least possible quantity of chemically pure nitric acid, and add to it an equal amount of acetic acid of ordinary strength; dilute to 8 or 10 times its volume, and filter if necessary. To the solution to be tested add sufficient sodium hydrate to render it strongly alkaline, then add a drop or two of the bismuth solution; heat to boiling and continue the boiling for a short time (20 to 30 seconds). If sugar is present, the white flocculent precipitate which formed on the addition of the bismuth solution to the alkaline liquid will become gray or black. The depth of color of the precipitate depends on the amount of sugar present. If the amount of sugar be very small the gray or black precipitate forms slowly, and it is necessary to allow it to stand for some time (10 or 15 minutes). This reduction occurs in the cold after standing quietly for 24 to 48 hours.

The bismuth solution will remain unaltered, and can be diluted to any degree without the precipitation of the bismuth.

In comparative tests with solutions of glucose, this test proved quite as delicate as Fehling's or Trommer's copper tests, and it undoubtedly can be used in many cases with great advantage, especially in conjunction with the above well-known tests. If albumen is present it must be removed before applying the test for sugar.

A New Test for Gallic Acid.

Prepare a solution of ammonium picrate by adding to a dilute aqueous solution of picric acid, an excess of ammonium hydrate.

Add a few drops of this reagent to an aqueous solution of gallic acid, and there is produced, at first, a red color, which in a few seconds becomes a beautiful green; the depth of color depending on the amount of gallic acid present.

Pyrogallic and tannic acids produce, at first, a reddish color, but there is no further material change.

MIAMI MEDICAL COLLEGE OF CINCINNATI, O., *March* 22, 1880.

DETECTION OF HYDROCHLORIC ACID BY SULPHURIC ACID AND ACID POTASSIUM SULPHATE.

BY H. W. WILEY.

This well-known test is more conveniently made in the following way than by distillation in a retort as recommended by Fresenius and others. Two small beakers are used, the smaller of which will fit into the larger, leaving a space of two or three centimetres between the two bottoms. The chloride and chromate are well rubbed together and placed in the larger beaker, care being taken that none of the particles adheres to the side of the vessel.

A few drops of sulphuric acid are added, and the smaller beaker put in place. A lump of ice, and if necessary a little salt, is then placed in the smaller beaker.

The chlorochromic acid (so called) is given off at a very gentle heat and is readily condensed on the cold surface of the small beaker. If there is more than a mere trace of chloride a watch glass can be substituted for the inner beaker. After the reaction has ceased the small beaker is removed, and the usual test (ammonium hydrate) is applied.

I extend and modify this test in the following ways:

1. After adding a drop of ammonia to the chromium oxychloride (still on the bottom of inverted beaker) acetic acid is added in excess. A drop of lead acetate is then added. Lead chromate is precipitated. This will detect hydrochloric acid when so little is present that the change of color with ammonia is not perceptible.

2. This is an easier and far more delicate reaction. In fact it seems quite as delicate and far more striking than the test with silver nitrate. The chromium oxychloride is prepared as above. With a stirring rod a fraction of a drop of sulphuric acid is placed in a porcelain dish, and by its side a minute crystal of strychnia. The stirring rod is then touched with the oxychloride, and this is stirred with the sulphuric acid and strychnia. The "color test" for strychnia is developed with even greater brilliancy than with potassium pyrochromate. The merest trace of a chloride is most unmistakably revealed by this test.

If bromides are present they do not at all interfere with the above reaction. Bromine itself with strychnia and sulphuric acid will not give the color test. If bromides are present, moreover, it is not difficult to detect them at the same time with the chlorides. The bromine formed is readily condensed and can be then easily detected. With iodides the case is quite different. In many cases I have found no trace of chromium oxychloride when both chlorides and iodides are present. At other times, the iodine which is set free seems to be dissolved in the oxychloride. In such cases on adding ammonia to the reddish yellow liquid, the whole mass turns black from the formation of iodide of nitrogen. On filtering this off the reactions for the chloride can be obtained in the filtrate, but without exactness. The iodide of nitrogen on the filter paper will, when dried, explode spontaneously, or when scratched or jarred. Prepared in this way the iodide of nitrogen appears to be of a better quality than that prepared by the ordinary methods.

I have yet to investigate the order of succession of the phenomena above mentioned as influenced by varying proportions of the several substances in the mixture. I have not been without a suspicion that bromides might possibly give rise to a trace of chromium oxybromide when treated as described. I have not, however, been able to procure an absolutely pure bromide with which I could subject the matter to the test of experiment. All the authorities, however, which I have consulted, agree that only pure bromine is produced. The bromides I have tried have all given faint reactions by the strychnia test, but I cannot say that they do not contain a trace of chlorine. If some one in possession of an absolutely pure bromide would make the experiment the result would be of interest. I am still investigating the anomalies produced by the admixture of iodides.

LAFAYETTE, INDIANA.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

V.—EXPERIMENTS IN THE PARA SERIES.

By Ira Remsen and Lyman B. Hall.

In the second paper of this series a substance was mentioned* incidentally which was obtained from coal-tar xylene as a secondary product in the preparation of the sulphamides. This was examined to a sufficient extent to warrant the conclusion that it is a derivative of paraxylene. It was converted by simple reactions into paratoluic and terephthalic acids, so that there could be little doubt in regard to its nature. It was also subjected to oxidation and thus converted into a monobasic acid, sulphamineparatoluic acid, the structure of which, however, was not determined by experiments. The belief was expressed that in the acid the sulphamide group would be found to be in the meta position with reference to the carboxyl, and in the ortho position with reference to the methyl. The question as to the structure of the acid has now been satisfactorily answered and the prediction shown to be correct. The details of the investigation are herewith communicated.†

Oxidation of Paraxylenesulphamide.

The sulphamide of paraxylene, separated from the mixture obtained from commercial xylene, was treated with the ordinary chromic acid oxidizing mixture, the proportions used being these:—

7.5 grams amide, 20 grams potassium pyrochromate, and 30 grams concentrated sulphuric acid diluted with three times its own volume of water. This mixture was heated gently for several hours, six to eight being usually sufficient. On cooling, a crystallized mass separates and increases in quantity for some time. This is now filtered off and washed with cold water, until the wash-water passes through uncolored. In order to separate the new acid from any amide which may have escaped the action of the oxidizing mixture, the whole mass is dissolved in dilute sodium carbonate and the solution evaporated down to a small volume.

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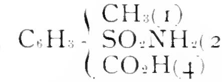
* This Journal, 1, 137.

† The experiments, as far as paraxylene itself is concerned, were performed by Dr. M. W. Iles.

On cooling, the amide crystallizes out. After separating the amide, the acid is precipitated by the addition of hydrochloric acid. The precipitated acid is again filtered and washed, and now recrystallized from water. It is thus obtained in the form of crystals, which have every appearance of purity. It fuses instantly at 267° (uncorrected).

The method of formation of the acid, taken together with the analyses of its salts communicated below, shows clearly that it is sulphamineparatoluic acid.



Sulphamineparatoluic acid, $C_6H_3\left\{\begin{array}{l}CH_3(1)\\ SO_2NH_2(2)\\ CO_2H(4)\end{array}\right.$, is very difficultly soluble in cold water, comparatively easily in hot. It crystallizes from an aqueous solution in beautiful large crystals of a silken lustre, which fuse at 267° (uncorrected) and 274° (corrected). It is very readily soluble even in cold alcohol. It is insoluble in ether, hot as well as cold. It crystallizes from alcohol in fine concentrically arranged needles, shorter than those obtained from water. From concentrated aqueous solutions there sometimes separate, together with the needles, verrucous masses which led at first to the suspicion that two products had been formed. On recrystallizing these masses, however, from more dilute solutions they separated in the same beautiful needles as the principal portion, and fused at exactly the same point.

Barium sulphamineparatoluate, $(C_6H_3.SO_2NH_2.CH_3.CO_2)_2Ba + 2H_2O$, was prepared from the free acid by boiling with barium carbonate. It crystallizes in concentrically arranged needles which are easily soluble in water. The crystals always attach themselves firmly in hard clumps to the beaker. After drying in the air it was analyzed.

I. 0.2302 gram lost 0.0132 gram H_2O at 200°, and gave 0.0890 gram $BaSO_4$ = 0.052332 gram Ba.

II. 0.359 gram lost 0.0218 gram H_2O at 200°, and gave 0.1385 gram $BaSO_4$ = 0.082438 gram Ba.

		Calculated.		Found.	
				I.	II.
$(C_8H_8SNO_4)_2$	...	428	71.21	...	..
Ba	...	137	22.80	22.73	22.96
$2H_2O$	...	36	5.99	5.73	6.07
		601	100.00		

Calcium sulphamineparatoluate, $(C_6H_3.SO_2NH_2.CH_3.CO_2)_2Ca + 4H_2O$, was prepared by boiling the acid with finely powdered Iceland spar. It is easily soluble in water, and crystallizes from the concentrated solution in very compact, radiating needles, which have a mother-of-pearl lustre. The air-dried salt was analyzed.

I. 0.1950 gram salt lost 0.026 gram H_2O, and gave 0.05 gram $CaSO_4$.

II. 0.22325 gram salt lost 0.02975 gram H_2O, and gave 0.05725 gram $CaSO_4$.

		Calculated.		Found.	
				I.	II.
$(C_8H_8SNO_4)_2$	...	428	79.26	...	...
Ca	...	40	7.41	7.55	7.54
$4H_2O$	...	72	13.33	13.33	13.33
		540	100.00		

Manganese sulphamineparatoluate, $(C_6H_3.SO_2NH_2.CH_3.CO_2)_2Mn + 5H_2O$, was prepared from the acid and manganese carbonate. It crystallizes in small needles from water, in which it is readily soluble. The salt was analyzed after being dried in the air.

I. 0.1785 gram salt lost 0.02825 gram H_2O, and gave 0.02425 gram Mn_3O_4.

II. 0.167 gram lost 0.02525 gram H_2O, and gave 0.02175 gram Mn_3O_4.

		Calculated.		Found.	
				I.	II.
$(C_8H_8SNO_4)_2$	...	428	74.70	...	...
Mn	...	55	9.60	9.79	9.67
$5H_2O$	...	90	15.70	15.83	15.59
		573	100.00		

Oxidation of Cymenesulphamide.

As the preparation of pure paraxylene in quantity involves considerable difficulty, it appeared advisable to employ in our experiments some other hydrocarbon belonging to the para-series. Recent experiments, particularly those of von Gerichten,[*] have shown that, when chlorine, bromine, nitric acid and sulphuric acid act directly upon cymene, they replace a hydrogen-atom situated in the ortho-position with reference to the methyl-group, and that

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[*] Berichte d. deutsch. chem. Gesell. 11, 1586.

the substitution-products thus obtained yield, by oxidation, derivatives of paratoluic acid in which the methyl-group still occupies the ortho-position with reference to the substituting atom or group. It hence seemed probable that by starting from cymene the same sulphamineparatoluic acid would be obtained as that described above and obtained directly from paraxylene itself. Experiment confirmed this view, and we were thus enabled to prepare sulphamineparatoluic acid without difficulty and in large quantity.

Pure cymene was heated on a water-bath with an equal volume of common concentrated sulphuric acid, a little fuming acid being finally added to effect complete solution. The amide was made from the sodium salt of the sulphonic acid, and was found to possess the properties ascribed it by Berger* and by Jacobsen.† The fusing point was, however, found to be constant at 113-114° (*uncorrected*), whereas previous observers have found it to be 112°.

The purified cymenesulphamide was treated with the chromic acid mixture in the following proportions: 1 part amide, 5 parts potassium pyrochromate and 7 parts concentrated sulphuric acid diluted with three times its volume of water. The mixture was heated for about three hours, first on the water-bath and finally over a free flame. On cooling the oxidation-product separated out, looking exactly like that obtained from paraxylene. The liquid was diluted and filtered. There was obtained upon the filter a mixture consisting of white needles and greenish, apparently amorphous lumps. The mass was treated several times with a cold dilute solution of sodium carbonate until nothing remained but the green lumps. Hydrochloric acid precipitated from the alkaline solution a white substance which was purified by recrystallization from water. The product is thus obtained in the form of long colorless needles fusing at 267° (uncorr.) and having all the properties of sulphamineparatoluic acid as described above.

The green lumps referred to appear to be a peculiar compound of the amide with oxide of chromium. Alcohol dissolves the substance completely, forming a green solution. On the addition of water to this solution a precipitate is formed. As the substance did not present strong evidence of its own purity it was not analyzed. It is insoluble in hydrochloric acid. If the alcoholic solution be boiled for a long time with a large amount of water, and then filtered, a colorless solution is obtained and this yields the pure

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* Berichte d. deutsch. chem. Gesell. 10, 976.

† Annalen der Chemie, 184, 194.

amide. The green residue is now soluble in hydrochloric acid. This indicates that the green compound though not decomposed by hydrochloric acid is broken up if boiled with a large quantity of water.

The only products formed by oxidation of cymenesulphamide are sulphamineparatoluic acid and the compound of the amide with chromium oxide.

Transformation of Sulphamineparatoluic Acid into the corresponding Oxy-Acids.

As Flesch has shown[*] that the sulphonic acid obtained by direct action of sulphuric acid in cymene yields an oxytoluic acid identical with one subsequently prepared by von Gerichten[†] and called by him α-oxyparatoluic acid, it was in the highest degree probable that our sulphamineparatoluic acid would yield the same oxy-acid when fused with potassium hydroxide. The fusion was performed in the usual manner in a silver crucible. On dissolving the mass in water and adding hydrochloric acid a precipitate was formed. This was dissolved in a large amount of boiling water, in which it was found to be very difficultly soluble, some animal charcoal added and the solution filtered. After several crystallizations the substance was obtained in the form of a white crystallized powder. This does not fuse at 300°, but sublimes somewhat above this temperature without fusing. With ferric chloride its solution gives a violet-red color. These properties are the same as those given by Burkhardt[‡] for oxyterephthalic acid. A close comparison showed that the two substances are identical. Oxidation of the oxytoluic acid is thus seen to be effected by the fusing potassium hydroxide.

The mother-liquor from which the oxyterephthalic acid is precipitated by hydrochloric acid yields on evaporation to a small volume a substance crystallized in needles. This was purified by boiling with animal charcoal and recrystallizing, and then converted into the corresponding lead salt, which was recrystallized from water and easily obtained pure. The salt crystallizes in long, transparent needles having a brilliant lustre. It corresponds to the lead salt of oxyparatoluic acid first prepared by Flesch[§] and more recently by von Gerichten.[||] The analyses of the salt showed, however, that, as obtained by us, it contains 1½ molecules of water of crys-

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[*] Berichte d. deutsch. chem. Gesell. 6, 481.

[†] Ibid. 11, 1586.

[‡] Ibid. 10, 144.

[§] Loc. cit.

[||] Loc. cit.

tallization instead of 2 as found by von Gerichten. It must be remarked that the only analyses of this salt hitherto published by von Gerichten do not give results agreeing very closely with those calculated for 2 molecules of water. The calculated percentage of water for a salt containing 2 molecules is 6.61, while von Gerichten found* 5.85 and 6.04 per cent. A salt with 1½ molecules requires 5.04 per cent. and with this the results of our analyses agree very closely.

I. 0.24 gram salt lost at 130° 0.012 gram H_2O and gave 0.13485 gram $PbSO_4$.

II. 0.2033 gram salt lost at 130° 0.0104 gram H_2O.

		Calculated.		Found.	
				I.	II.
$(C_8H_7O_3)_2$	...	302	56.34	...	...
Pb	...	207	38.62	38.38	...
$1\frac{1}{2}H_2O$	...	27	5.04	5.00	5.11
		536	100.00		

The acid was separated from the salt and found to fuse at 205° (*uncorrected*), while von Gerichten and Rössler state it to be at 203-204°. It crystallizes in needles which are difficultly soluble in cold, but easily soluble in hot water. Ferric chloride produces no color in its solution. It is difficultly volatile with water vapor. From a careful comparison of the acid with the α-oxyparatoluic acid now known, we can conclude that the two are undoubtedly identical. But von Gerichten† has shown that in α-oxytoluic acid, the hydroxyl group is in the ortho position with reference to the methyl group. Hence it follows, that in sulphamineparatoluic acid the sulphamide group and the methyl are in the ortho position with reference to each other, while, as the acid is derived from paraxylene, it further follows that the methyl and carboxyl are in the para position with reference to each other.

The structure of the acid is thus found to be in accordance with the view expressed when the substance was first discovered, and another illustration is given of the correctness of the law which lies at the foundation of the phenomena which are here being subjected to investigation. *The negative group protects the hydrocarbon residue*, preventing its oxidation by chromic acid.

Another curious conclusion which this investigation helps to

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* Berichte d. deutsch. chem. Gesell. 11, 706.

† Loc. cit.

establish, though full attention has previously been called to the subject by von Gerichten, is that when negative groups enter into cymene, they take the meta position with reference to the larger residue, propyl. This has been found to be true of Cl, Br, NO_2, SO_2OH. In one of the earlier papers[*] of this series attention was called to a similar fact in connection with paraethyltoluene. It was shown that when bromine acts upon this hydrocarbon, and the product oxidized, a bromparatoluic acid is obtained. The belief was expressed that in this case it would be found that the bromine exerts a protective influence upon the methyl group. The subsequent determination of the structure of the bromparatoluic acid proved the correctness of the first belief.

Sulphoterephthalic Acid.

The experiments in the meta-series have shown that when the monobasic sulphamine acid is treated with potassium permanganate in neutral solution, the sulphamide group is converted into the sulpho-group and a tribasic acid, sulphoisophthalic acid, is formed It was hence thought probable that sulphamineparatoluic acid would, under the same treatment, yield sulphoterephthalic acid. Indeed a salt very similar to the acid potassium salt of sulphoisophthalic acid was found in the residues from the oxidation of the mixture of xylenesulphamides, and the same salt was again obtained when a little sulphamineparatoluic acid was subjected to the action of potassium permanganate. The nature of the salt was not determined, however, owing to a lack of material. It has now been prepared in larger quantity and its nature determined. It is *sulphoterephthalic acid.*

The substances were brought together in the following quantities: 1 gram sulphamineparatoluic acid, 5 grams potassium permanganate and 100 c. c. water. The mixture was heated in a flask on a water-bath for about 7 to 8 hours. There remained a slight excess of the permanganate which was reduced by means of a few drops of alcohol. The solution was then filtered, concentrated and treated with hydrochloric acid. A white crystalline precipitate was formed. This was recrystallized from water and thus easily obtained in perfectly pure condition. From a concentrated solution it crystallizes in long transparent needles, from a dilute solution it separates in well-developed plates which are large enough to admit

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[*] On the Oxidation of Bromparaethyltoluene. This Journal, 1, 138.

of measurement. The salt is difficultly soluble in cold water, particularly if hydrochloric be present, though in warm water it is quite easily soluble. The substance was repeatedly tested for nitrogen by fusing it with sodium and then treating with a partially oxidized solution of ferrous sulphate. Not a trace of a blue precipitate was obtained from the purified salt, and the conclusion is justified that it contains no nitrogen. The analyses gave the following results:

I. 0.3018 gram lost at 150° 0.0182 gram H_2O, and gave 0.0867 gram K_2SO_4.

II. 0.6641 gram lost at 150° 0.0399 gram H_2O, and gave 0.1916 gram K_2SO_4

		Calculated.		Found.	
				I.	II
$C_8H_5O_7S$	...	245	81.10	...	...
K	...	39.1	12.94	12.89	12.95
H_2O	...	18	5.96	6.03	6.00
		302.1	100.00		

The results agree closely with those required by a salt of the formula, $C_6H_3\begin{cases}CO_2H\\CO_2H+H_2O\\SO_3K\end{cases}$, or *mono-potassium sulphoterephthalate.*

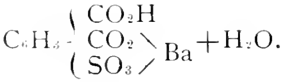
If this is really the formula of the salt, it must still contain two atoms of hydrogen replaceable by metals. To decide this point, weighed quantities of the salt were neutralized with an ammonia solution of known strength.

I. 0.4739 gram salt required for neutralization 31.2 c. c. of an ammonia solution of known strength. The quantity required according to calculation is 30.8 c. c.

II. 0.6101 gram required 39.4 c. c. of the same ammonia solution, whereas the calculated quantity for this amount of salt is 39.6 c. c.

The results of the analyses, and the neutralization experiments taken together with the method of formation, show clearly that the substance under examination is a derivative of sulphoterephthalic acid. The permanganate in this case, as well as in the meta series, converts the methyl group into carboxyl and the sulphamide group into the sulpho-group.

Monohydro-barium sulphoterephthalate,



$$C_6H_3\left\{\begin{array}{l}CO_2H\\ \left.\begin{array}{l}CO_2\\ SO_3\end{array}\right\rangle Ba\end{array}\right. + H_2O.$$

This salt is thrown down in crystalline form when a solution of barium chloride is added to a solution of the potassium salt just described. It is very difficultly soluble in water, hot as well as cold. It cannot be obtained in well-crystallized form from an aqueous solution, though it looks homogeneous and crystalline. A similar salt of sulphoisophthalic acid, containing 1½ molecules of water, was described in an earlier paper. The analyses gave the results here communicated:

I. 0.40345 gram salt lost 0.01815 gram H_2O at 270° and gave 0.2307 gram $BaSO_4$.

II. 0.3246 gram salt lost 0.0148 gram H_2O at 290° and gave 0.1884 gram $BaSO_4$.

III. 0.263 gram salt gave 0.089964 gram $BaSO_4$.

		Calculated.		Found.	
$C_8H_4O_7S$	...	244	61.15	...	...
Ba	..	137	34.34	34.12	34.20
H_2O	...	18	4.51	4.55	...
		399	100.00		

The facts here communicated are sufficient for the present to characterize the new substance, but it will be subjected to further study in order that we may learn more concerning its intimate nature. Dr. William Burney has already investigated a number of its derivatives and has established beyond the possibility of a doubt the character of the relation which it bears to terephthalic acid. The results of his study will soon be published in this Journal.

Terephthalic Sulphinide.

If the *potassium salt* of sulphamineparatoluic acid be treated with potassium permanganate in the manner described above, the result is quite different from that reached when the free acid is used. The same is true if a few drops of a solution of potassium carbonate or hydroxide be added to the oxidizing mixture. Only a small quantity of ammonia is given off and the product contains nitrogen and potassium. The oxidation is conducted in exactly the same way as in connection with the free acid, and the final addition of hydrochloric acid produces a similar precipitate. This is more difficultly soluble in water than the acid potassium salt of sulphoterephthalic acid, and comes down in different forms. It crystallizes usually in short thick prisms, or from concentrated solutions it is thrown out in glistening flakes, which, however, increase in size as the solution becomes cool. Under some circumstances it crystallizes in forms which are very similar to those taken by the sulphoterephthalate, but, if the solution containing the crystals be allowed to stand for a few days, they pass over into the forms which are characteristic of the new substance.

In addition to the principal product containing nitrogen, only a small quantity of the sulphoterephthalate is formed. If, however, the free acid be oxidized none of the nitrogenous substance is formed, or, at least, none has been found up to the present, though special precautions have been taken for the purpose of finding it.

It was at first thought that the new product is simply a derivative of sulphamineterephthalic acid, $C_6H_3\left\{\begin{matrix} CO_2H \\ CO_2H, \\ SO_2NH_2 \end{matrix}\right.$ but it was soon shown that in all probability it is a substance similar to the one recently described by one of us (R) together with C. Fahlberg,* under the name benzoic sulphinide. This is an inner anhydride of orthosulphaminebenzoic acid, $C_6H_4\left\{\begin{matrix} CO \\ SO_2 \end{matrix}\right\rbrack NH$, obtained as one of the products of the oxidation of orthotoluenesulphamide with potassium permanganate. In sulphamineparatoluic acid there exist the same conditions as those in orthotoluenesulphamide, *i. e.* the sulphamide group occupies the ortho-position with reference to the methyl. Apparently the oxidation takes place in the same way in the two compounds. The analyses led to the following results:

I. 0.2715 gram salt lost 0.0179 gram H_2O at 240°, and gave 0.0831 gram K_2SO_4.

II. 0.5038 gram salt lost 0.0332 gram H_2O at 240°, and gave 0.1514 gram K_2SO_4.

III. 0.4338 gram gave 19.4 c.c. N at 766.5 m.m. pressure at 23.5°.

IV. 0.4315 gram gave 0.3445 gram $BaSO_4$.

V. 0.5204 gram gave 0.42495 gram $BaSO_4$.

In attempting to determine the formula of the substance from the experimental data here given, a difficulty is met with at once in

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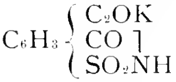
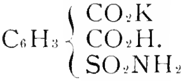
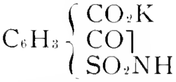
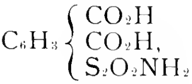
* This Journal 1, 426.

connection with the molecule of water which is given off at 240°. Is this to be regarded as water of crystallization? or is it due to the transformation of the original substance into an inner anhydride? If it is water of crystallization then the formula of the substance is  $C_6H_3\left\{\begin{array}{l}C_2OK\\ CO\,]\\ SO_2NH\end{array}\right.+H_2O$, and it is similar to the product which we have called benzoic sulphinide. If, however, the water is given off from the substance and an anhydride formed, then the formula is  $C_6H_3\left\{\begin{array}{l}CO_2K\\ CO_2H.\\ SO_2NH_2\end{array}\right.$ We believe that the former view is the more probable, for the reason that, in the case of an isomeric substance belonging to the meta series since obtained,* there are two molecules of water given off together under the same conditions, and, in the light of a simpler explanation, it would be purely gratuitous to assume that one of these molecules represents water of crystallization, and the other water of constitution. The comparison of the results of the analysis with the results calculated for two possible formulas is given below, assuming in each case that there is a molecule of water of crystallization present:

		Calculated for $C_6H_3\left\{\begin{array}{l}CO_2H\\ CO_2K\\ SO_2NH_2\end{array}\right.+H_2O$	Found.		Calculated for $C_6H_3\left\{\begin{array}{l}CO_2K\\ CO\,]\\ SO_2NH\end{array}\right.+H_2O.$
K	...	12.98	13.74	13.49	13.81
N	...	4.64	5.04	...	4.94
S	...	10.62	10.95	11.21	11.30
H_2O	...	5.98	6.58	6.59	6.36

The formula which we ascribe to the substance is  $C_6H_3\left\{\begin{array}{l}CO_2K\\ CO]\\ SO_2NH\end{array}\right.+H_2O$. According to the principle of nomenclature adopted in a previous paper this is the potassium salt of *terephthalic sulphinide*, or, in order to indicate in the name the acid properties, it might be called *sulphinido-terephthalic acid.* Of course this anhydride readily yields salts of sulphamineterephthalic acid,  $C_6H_3\left\{\begin{array}{l}CO_2H\\ CO_2H,\\ S_2O_2NH_2\end{array}\right.$ hence the potassium salt when dissolved in water must contain a second hydrogen atom replaceable by metals.

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* Berichte d. deutsch. chem. Gesell. 12, 1436.

That this is so was conclusively proved by three neutralization experiments.

I. 0.54935 gram required for neutralization 19 c. c. of an ammonia solution of known strength.

II. 0.5526 gram required 19.8 c. c.

III. 0.3972 gram required 14.4 c. c.

These results, when compared with the calculated quantities for the two possible formulas, again show that, if the questionable molecule of water be regarded as water of crystallization, the substance is undoubtedly a derivative of the sulphinide.

Calculated for $C_6H_3\left\{\begin{matrix}CO_2H\\CO_2K\\SO_2NH_2\end{matrix}\right. + H_2O.$	Used.	Calculated for $C_6H_3\left\{\begin{matrix}CO_2K\\CO]\\SO_2NH\end{matrix}\right. + H_2O.$
17.9 c. c.	19.0 c. c.	19.0 c. c.
18.3 c. c.	19.8 c. c.	19.3 c. c.
13.1 c. c.	14.4 c. c.	14.4 c. c.

Facts which have been discovered in this laboratory since the above investigation was completed indicate very clearly that the nitrogenous substance obtained, when the oxidation is carried on in an alkaline solution, in reality belongs to the class of bodies designated as sulphinides, and it seems to be a general law that:

Whenever a compound containing the sulphamide group and methyl in the ortho position is oxidized in *alkaline solution*, a sulphinide is formed.

If, on the other hand, the solution is *neutral at the beginning of the oxidation*, as it is when orthotoluenesulphamide is employed, then two products are formed in about equal quantities. One of these is the sulphinide and the other the corresponding sulphonic acid.

If, finally, the solution is *acid at the beginning of the operation*, as it is when free sulphamineparatoluic acid is oxidized, only the corresponding sulphonic acid is formed.

The last result is also reached apparently, if precautions be taken to prevent the formation of free alkali. Thus, in an experiment performed by Dr. Fahlberg, the oxidation was carried on in a vessel through which a constant current of carbon dioxide was conducted. The result in this case was the same as in those cases in which free acids were employed. Complete transformation into the corresponding sulphonic acid took place. According to this, we can control the nature of the product by very simple means. If, in oxidizing with potassium permanganate a sulphamide compound containing a hydrocarbon residue in the ortho position, we desire the corresponding sulphinide, a little potassium carbonate or hydroxide is added to the oxidizing mixture. If we desire the sulphonic acid, precautions must be taken to prevent the formation of free alkali, at least at an early stage of the process, and the simplest way to prevent this is to keep the vessel filled with carbon dioxide. These general statements are, it must be confessed, based on too small a number of experiments to warrant their final acceptance without further verification. It is hoped that experiments now in progress in this laboratory will furnish the required testimony.

April, 1880.

REVIEWS AND REPORTS.

Brief Review of the most important Changes in the Industrial Applications of Chemistry within the last few Years.

(Continued from Vol. I, p. 449.)

Manufacture of Glass.

Materials.—Improvement has of late years been observable in the more general use of comparatively pure materials, even the sand being, in consequence of cheapened transportation, more carefully selected than formerly; but especially have the alkalies been obtainable in much purer forms and at lower prices. As the result of this, colorless glass has noticeably replaced for many common purposes, as in the case of most apothecaries' bottles for dispensing medicines, perfumery, etc., the coarser "green glassware" formerly in use. There has also been improvement in the pains bestowed upon ascertaining and using the best proportions of the materials with a view to homogeneity and definiteness of composition in the glass, thus diminishing the risk of "devitrification" and ready alteration of the surface of the glass in use by water or other reagents. There seems, however, to be still room for advance in this direction, both as to investigation and application of its results in practice. Of comparatively new materials used, zinc oxide in Belgium and barium carbonate in France and the north of England hardly deserve to be considered as more than experimental additions.

Furnaces.—Decidedly the most important improvement made for a long time in the manufacture of glass has been the adaptation to this special use of the Siemens regenerative furnace with gaseous fuel. Originally arranged to work with glass pots of the types long in use, the furnace in its improved form, designed by Siemens, dispenses with the use of these vessels altogether, thereby saving much expense, labor and risk, and provides for the complete preparation of the glass in the hearth itself, this being divided into three compartments, in the first of which the mixture of raw materials is fused, in the second the glass is "fined" or cleared, and in the third it is brought down to the proper temperature and therefore consistence for working.

Except perhaps iron puddling and steel making, no application of this valuable invention brings out more prominently its peculiar merits — the continuous action, crude material going in at one end and finished glass coming out of the other; the purely gaseous atmosphere of the hearth, free from soot or ash; the extremely high temperature readily obtainable, affording the means of perfect fusion and easy separation of sand grains, gas bubbles, &c.: the effective mixture of the molten glass as it flows under and over the partition walls of the hearth; and the complete command of temperature for working purposes, both of the glass itself and of the working openings for reheating.

Processes of Glass Working.—For the production of glass in sheets for windows, the "crown glass" process of "flashing," long a distinctively English industry, has almost completely ceased to be employed, while in its place the "cylinder" process has undergone marked extension and improvement as to the scale upon which its product is turned out, the size of the sheets made by it—reaching even to 84x42 inches — and the smooth, even condition of the surface of the flatted sheets. Plate glass too has been brought more and more widely into use, both in the original form of sheets polished on both sides after casting, and perhaps still more largely with rough surfaces as taken from the casting table, and with flutings and other figures embossed, or perforations made beneath the roller. Immense plates, extending up to more than 20x10 feet, have become familiar to us, the limit of size being found in fact more in the difficulty of safely moving and setting in place such magnificent slabs than in that of originally producing them. In the manufacture of hollow ware perhaps the most noteworthy change has been the growth of the process of pressing in moulds without blowing. The development of this especially American industry has been rapid, and marked by much varied ingenuity as to the details of the moulds and other tools.

Annealing.—Beside minor improvements in the construction of kilns for ordinary annealing with movable soles or floors, a marked novelty has been the introduction by De la Bastie and others of the practice of rapid cooling of articles of glass to a temperature still much above that of the atmosphere, giving rise to the manufacture of the so-called "hard glass" or "toughened glass," in the production of which the articles to be treated are, at a low red heat or a temperature just low enough to secure rigidity, plunged suddenly into a bath of heated oil, glycerine or other suitable material.

The process of Pieper, involving exposure of the hot glass to a current of superheated but colder steam, and that of F. Siemens, forcing the glass into hollow moulds, generally of metal, kept at determinate temperatures in their different parts by the circulation of water, while actual contact with the face of the mould is prevented by the interposition of a layer of wire gauze or other material, produce essentially the same sort of effect. For some purposes the resulting great increase in strength of the glass, its capability of withstanding greater mechanical stress and more violent blows, is undoubtedly valuable, but it seems likely that the expectations at first entertained as to the usefulness of the new product will turn out to have been exaggerated. Its unmanageable character as to any modification of dimensions, shape or surface by cutting with a diamond or by grinding, its complete, even dangerous, shattering when it does break, and the difficulty of securing uniform results from the tempering under varying conditions of size and shape of the articles treated, are all serious disadvantages, though perhaps not altogether incapable of being overcome by further modifications of the process. The very recent and rather startling proposal of F. Siemens to make railway sleepers of toughened glass, aside from any special difficulties or dangers, does not seem likely to be altogether free from the same objections arising from excessive jarring vibration and consequent wear and tear of rails and rolling stock, which caused the granite blocks used in the early days of railway construction to be laid aside.

Optical Glass.—The progressive improvement in this difficult branch of the manufacture, continued for a good many years past and still going on, is best evidenced by the steady increase in the size of the disks, now obtainable up to more than thirty inches in diameter, from which the largest telescope lenses are made, while clearness, uniformity and freedom from flaws of any kind of these great lenses have also been secured in higher degree than formerly. Chemically the chief novelty in the composition of this kind of glass has been the introduction of thallium silicate into flint of unusual density, but this has been practised upon a very limited scale only.

Decoration of Glass Work.—There has been of late years some advance in the clearness and brilliancy of colored glass for windows, but more marked results have been attained in the artistic than the technical treatment of this material. The revived imitations of the *defects* of ancient colored glass, such as imbedded sand-grains, air bubbles and the like, form a curious feature of its recent history.

The imitations in glass of the various precious stones are made of late with remarkable fidelity to natural appearance, and some of the specimens sold are noticeable for a degree of hardness, much less, it is true, than is usually claimed for them by dealers, but much exceeding anything that was known some years ago.

Well deserving the attention they have received have been the beautiful products of the revived glass industry at Murano, especially the delicate "ritorto" work, depending on the plastic union of symmetrically disposed rods of variously colored glass and the twisting of the mass they produce as it is afterwards developed into the desired form. Not only under Salviati at Murano, but more recently in Austria has this mode of decoration been admirably applied to the reproductions of early forms as well as to designs of modern origin.

To the older varieties of "milk glass" or enamel has been added the "hot-cast porcelain" made by fusing together quartz sand, cryolite and zinc oxide, chiefly used so far for the rougher and less artistic articles which admit of being made from such material.

In surface enamelling of sheet glass may be noted the transfer of lace patterns from the woven or netted fabric itself, used as a stencil to distribute the pulverized enamel upon the surface, afterwards to be burnt on.

The most valuable novelty in the surface alteration of glass is the process of etching by means of Tilghman's sand-blast. The simplicity and quickness of the process, the great depth to which the abrasion of the glass may readily be carried, cutting through, for instance, a flashing of colored glass or even producing complete perforation, the applicability of the method to sheets of glass so large as to be treated with great difficulty, if at all, by the older grinding-wheel or by hydrofluoric acid, and the delicacy with which the minute features of intricate designs may be engraved — admirably shown in some of the etchings of photographs upon a film of chromated gelatine covering the glass — approve the process as one of great and permanent value.

Amongst the latest modifications of glass decoration is the "iridescent glass" exhibiting a delicate play of soap-bubble colors, the result of slight chemical attack of the surface by moderately strong liquid hydrochloric acid under pressure in close vessels, or by the fumes from chloride of tin or analogous material volatilized in a reheating furnace.

The silvering of glass by deposition of metallic silver from its solutions by means of such reducing agents as glucose, milk sugar, aldehyde, tartaric acid, etc., has completely passed from the laboratory to the workshop, where it is now regularly and extensively practised. A somewhat recent improvement consists in increasing the density of the film of silver, and at the same time removing the unpleasant yellow tinge which it is apt to have, by moistening the surface with a dilute solution of mercuro-cyanide of potassium, so as to form a silver amalgam.

Dodé's process for platinizing glass, by carefully heating it after the surface has received a nicely applied thin coating of platinic chloride mixed with one of the essential oils, has the advantage of furnishing a mirror which reflects from the front face, avoiding the double passage of light through the glass itself, while the exposed metal is not liable to tarnish. It does not seem to have been generally noticed that a simple piece of flat sheet glass treated in this way, and supported at a suitable inclination, makes quite an effective *camera lucida*, as the platinum film is thin enough to permit of the pencil and hand of the draughtsman being seen through it, while at the same time the objects to be copied are seen by reflection.

Glass drawn out into extremely fine threads—the so-called "glass wool"—has of late, in the hands of a Viennese firm, been used for decorative purposes of a better sort than the long known toys turned out at the glassblower's lamp, and has also been produced in useful shape as a material for filtration.

MANUFACTURE OF PORCELAIN AND OTHER CLAY-WARE.

It is more difficult to point out marked changes in this industry than in that of glass in matters connected with chemistry: the materials used being mixtures of more complex character, and the extent and manner of their union in the baking varying with the mode in which the heat is applied, the chemistry of both processes and products is less advanced. More attention has been given to mechanical improvements in grinding, mixing, etc., to the methods of burning, and especially to artistic expression in design and decoration. Still progress has unquestionably been made in the former direction within the last few years.

General Character of Products.—On the whole, probably the greatest improvement has been in the higher grades of stoneware and earthenware, rather than in porcelain itself. Almost the same care bestowed upon the production of the latter has of late been given to the treatment of the former, the selection of the materials, their subdivision, careful kneading together, moulding, drying, burning and glazing. Special kinds of ware have attracted particular attention from time to time, partly from the intrinsic character of the mass, partly from the designs which it has been used to carry out, such as the revived Majolica and Persian ware of Minton and the Parian and other biscuit ware of Copeland and others. The excellent common stoneware now made, strong and capable of bearing much in the way of change of temperature and exposure to energetic chemical reagents, has done valuable service as material for many of the vessels used in manufacturing chemistry.

Mechanical Appliances.—The most valuable of these brought into use in comparatively recent times has probably been the strong and effective filter press, which has done so much good service in connection with general chemical manufactures, and which is now largely used in removing the surplus water from the clay after the process of mixing. Special features introduced in some of these presses tend to prevent as far as possible the enclosure of air bubbles, which would lead to flaws in the ware when burnt.

Kilns.—The regenerative gas furnace has begun to lend its valuable aid to this manufacture as well as to that of glass, and with marked advantage, including much saving of fuel and reduction of the number of pieces of ware spoiled in the firing. In this application of the furnace there is room for careful study of the distribution of the heat, dependent on the arrangement of the gas and air flues, in order to secure uniformity of firing throughout the contents of the kiln, varying as these do in form and size.

Decoration.—The feature of most note in this direction has of late perhaps been the extension of the transfer of *printed* patterns and designs, replacing to a large extent painting by hand. The method in question has long been in use for coarser purposes, but now much better work is done, and the production of effects in several colors by the well-known method of superposition—"color printing"—is commonly and extensively practised. Metallic "lustres" too are applied with more successful effect than formerly, and the peculiar surface appearance, resembling that of mother-of-pearl, given by a lustrous bismuth glaze, has been introduced.

J. W. Mallet.

(*To be continued.*)

Report on Progress in Analytical Chemistry.

(*Continued from p.* 367.)

Hydrogen.—W. Hempel* finds that the free hydrogen contained in any mixture of hydrogen, marsh gas and nitrogen can be determined by mingling with air and conducting the mixture over superficially oxidized palladium sponge. If care is taken to keep the temperature below 200°, the marsh gas is wholly unaffected, while the free hydrogen is completely oxidized.

A. Lionel† recommends the use of the black oxide of copper for the purification of hydrogen gas. It completely arrests, even at ordinary temperatures, hydrochloric acid, and the compounds of hydrogen with sulphur, selenium, phosphorus, arsenic, antimony and silicon, but not the hydrocarbons. The oxide to be used for this purpose is best prepared by treating the sulphate of copper with caustic potassa and drying the precipitate at 100°.

Oxygen.—F. Fischer‡ describes an apparatus for the determination of the oxygen of the air by means of heated copper wire.

F. Tiemann and C. Preusse§ describe in detail, and with some modifications of their own, the three methods which have been proposed for the quantitative determination of the oxygen absorbed

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* Ber. d. d. ch. Ges. 1879, 1006.

† Comptes rendus, 89, 440.

‡ Ber. d. d. ch. Ges. 1879, 1696.

§ Ibid. 1879, 1768.

in water; namely, the gas-volumetric, the volumetric of Schützenberger and Risler, and that of Mohr. They also give the results which they obtained by a comparative examination of the three. The quantities obtained by the first two are nearly equal and quite correct, while those by the last are uniformly too small.

Water.—H. Pellet[*] describes his method of determining the several varieties of nitrogen contained in natural waters. It is similar to that lately proposed by Lechartier.[†]

F. Tiemann and C. Preusse[‡] have brought together again the several methods in use for the estimation of the organic matter in water. Their own experiments tend to prove the superiority of Kubel's method over that of Fleck; also, that organic matter in considerable quantities is lost during the evaporation of an impure water.

Chlorine.—R. Nolte[§] states that when grains are incinerated, a part and in some cases the whole of the chlorine is lost in consequence of the decomposition of the chlorides by phosphoric acid. To remedy this the author incinerates in the presence of carbonate of sodium.

G. Fraude[||] recommends perchloric acid as a reagent for the detection of certain alkaloids.

Iodine.—O. Schott,[¶] "On the Determination of Iodine in Varec."

To determine iodine volumetrically E. Allary[**] employs a standard solution of bromide and bromate of potassium, instead of hyposulphite of sodium. The iodide against which the solution is to be standardized, or in which the iodine is to be determined, is treated with starch paste and hydrochloric acid, and the solution of bromide and bromate allowed to flow in from a burette. The hydrochloric acid, bromide and bromate react as follows:

$$5KBr + KBrO_3 + 6HCl = 3H_2O + 6KCl + 6Br.$$

The bromine thus liberated sets free an equivalent amount of iodine—$6Br + 6MI = 6MBr + 6I$. These reactions continue until the iodide has been completely decomposed, and at that point the blue color imparted to the starch attains its maximum intensity. If, now, more of the solution of bromide and bromate is added, the free bromine combines with the iodine and the blue color gradually diminishes to a minimum.

Sulphur.—J. Fletcher[††] states that sulphide of hydrogen may be easily prepared for laboratory purposes by fusing together sulphur and paraffine. W. Johnstone[‡‡] remarks that he made use of this method for some time, but gave it up in consequence of the explosive properties of the mixture.

C. Fahlberg[§§] has replied to Delachanal and Mermet,[||||] and

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[*] Comptes rendus, 89, 523.

[†] This Journal, 1, 285.

[‡] Ber. d. d. ch. Ges. 1879, 1906.

[§] Comptes rendus, 89, 955.

[||] Ber. d. d. ch. Ges. 1879, 1558.

[¶] Zeitsch. an. Ch. 18, 443.

[**] Bull. de la Soc. Chim. 32, 273.

[††] Chem. News, 40, 154.

[‡‡] Chem. News, 40, 167.

[§§] Ber. d. d. ch. Ges. 1879, 2303.

[||||] This Journal, 1, 288.

shown that the method devised by Iles and himself is essentially different from that proposed by these authors.

T. Nakamura[*] determines the sulphur in coal by mixing the finely pulverized material with carbonate of sodium or carbonate of sodium and potassium, and heating below redness. The coal is rapidly oxidized without evolution of smoke.

To determine the sulphur contained in sulphides A. Colson[†] burns in a current of oxygen, and absorbs the products of the combustion in a solution of caustic soda of known strength. This solution is afterwards diluted to a known volume, and the sulphite contained in a measured portion of it determined by means of iodine. To another equal portion sufficient iodine solution to convert the sulphite into sulphate is added, and the excess of alkali then estimated by means of standard sulphuric acid. Allowance is made in the calculation of results for the fact that each atom of iodine neutralizes one molecule of caustic soda:

$$2NaOH + I_2 + Na_2SO_3 = Na_2SO_4 + H_2O + 2NaI.$$

According to A. Rollet[‡] the sulphur contained in iron, steel, ores, slags and fuel can be readily and completely converted into sulphide of hydrogen by placing the material in a porcelain tube and heating it to redness in a current of gas, consisting of three-fourths of hydrogen and one-fourth of carbon dioxide. The author absorbs the sulphide of hydrogen thus produced in a solution of silver nitrate. When it is desired to determine the sulphur contained in a gas, the material is mingled with carbon dioxide or hydrogen according to the quantity of oxygen which it contains, and then passed through the heated porcelain tube.

Nitrogen.—H. Ritthausen,[§] "On the Nitrogen contained in Vegetable Albumenous Compounds, as determined by the Method of Dumas and that of Will and Varrentrapp."

A. R. Leeds,[||] "On the Determination of Nitrates in very dilute Solutions."

R. Warrington,[¶] "On the Determination of Nitric Acid by Means of Indigo, with special Reference to Water Analysis."

A. Wagner,[**] "On the Formation of Nitric Oxide by Decomposition of Saltpeter at red Heat."

E. Pfeiffer,[††] "On Persoz's Method of estimating Nitric Acid."

In order to detect nitric in the presence of nitrous acid, A. Piccini[‡‡] destroys the latter by means of urea and sulphuric acid. The solution may then be tested for nitric acid by adding zinc, iodide of potassium and starch.

J. Tschelzoff,[§§] "On the Determination of Nitrogen in Explosive Nitric Esters."

P. Griess[||||] has described a new reaction by which the minutest

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[*] Jr. Ch. Soc. 1879, 785.

[†] Bull. de la Soc. Chim. 32, 115.

[‡] Dingler's Jour. 233, 124.

[§] Z. an. Ch. 18, 601.

[||] Z. an. Ch. 18, 428.

[¶] Jr. Ch. Soc. 1879, 578.

[**] Z. an. Ch. 18, 552.

[††] Z. an. Ch. 18, 597.

[‡‡] Ber. d. d. ch. Ges. 1879, 1928.

[§§] Ber. d. d. ch. Ges. 1879, 1486.

[||||] Ber. d. d. ch. Ges. 1879. 427.

traces of nitrous acid may be detected. The solution containing the nitrite is acidified with sulphuric acid, and then treated with a small quantity of a solution of sulfanilic acid. After the lapse of about ten minutes a few drops of a solution of naphtylamine sulphate, from which the color has been removed by animal charcoal, are added. A fine red color is developed. By means of this reaction the presence of nitrous acid in the saliva may be detected.

Phosphorus.—E. Wein,[*] with the assistance of L. Rösch and J. Lehmann, has made a careful examination of the different methods proposed for the extraction of the soluble phosphoric acid in superphosphates; and concludes that the usual practice of digesting 20 grams of the material for two hours with one liter of cold water gives the best results.

O. Schlickum[†] proposes a new method for the alkalimetric determination of phosphoric acid, which is based on the fact that a solution of this acid containing cochineal becomes reddish-violet in color as soon as one atom of hydrogen in each molecule has been replaced by a metal.

Arsenic.—F. Selmi,[‡] "On Schneider's Method of Separating Arsenic in Cases of Poisoning."

Antimony.—F. P. Dewey,[§] "On Clarke's Method for the Separation of Tin from Arsenic and Antimony."

Bismuth.—M. Kuhara,[||] "A Method for Estimating Bismuth Volumetrically."

R. Schneider,[¶] "On the Conduct of Bismuth containing Arsenic towards Nitric Acid, and on the Preparation of basic Nitrate of Bismuth free from Arsenic."

Carbon.—S. Kern,[**] "On the Determination of Carbon in Cast-Steel."

W. D. Herman,[††] "On the Determination of Carbon in Steel."

J. C. Smith,[‡‡] "A Device for the rapid Filtration of the Carbon in Cast-Iron and Steel Analyses."

F. Landolph,[§§] "On the Analysis of organic Compounds containing Fluorine and Boron."

W. Hempel[||||] has made some experiments on the limits of the detection of carbonic oxide; and, incidentally, on the quantity of it required to produce symptoms of poisoning. Mice were placed between two funnels whose edges were fastened together by means of a rubber band, and air containing known percentages of carbonic oxide drawn through the apparatus. The blood of the animals was then subjected to spectroscopic examination as prescribed by Vogel. In this manner it was found possible to detect the carbonic oxide when the air experimented upon contained only .03 per cent. Decided symptoms of poisoning were observed as soon as the

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[*] Liebig's Annalen 198, 290.

[†] Ber. d. d. ch. Ges. 1879, 2253.

[‡] Ber. d. d. ch. Ges. 1879, 1699.

[§] This Journal, 1, 244.

[||] This Journal, 1, 326.

[¶] Jr. fur prak. Ch. 20, 418.

[**] Chem. News, 40, 225.

[††] Chem. News, 40, 263.

[‡‡] This Journal, 1, 368.

[§§] Ber. 1879, 1586.

[||||] Z. an. Ch. 18, 399.

proportion of carbonic oxide was increased to .05 per cent. Experiments were also made upon the spectroscopic detection of carbonic oxide in diluted blood, through which air containing it had been drawn. The latter method, however, was found to be less sensitive than the former. When the air contained less than .05 per cent. the blood failed to give the characteristic reaction.

A. Wagner[*] has found that when carbon dioxide is passed over heated stannous oxide, the former is reduced to carbonic oxide, and the latter oxidized to stannic oxide.

K. Birnbaum and M. Mahn,[†] "On the Conduct of Anhydrous Oxide of Calcium towards Carbonic Anhydride."

M. Kapusstin,[‡] also G. Lunge,[§] "On the Determination of the Carbon Dioxide of the Air."

A. Gawalovski,[||] "Gasvolumetric Estimation of Carbonic Acid."

Potassium.— H. Precht,[¶] "The Determination of Potassium as double Chloride of Potassium and Platinum."

W. Knop and Hasard,[**] "Determination of Alkalies in Silicates."

Lithium.—G. Merling[††] describes some experiments on the compounds of lithium with phosphoric acid, which tend to establish the accuracy of the method of determining lithium as phosphate.

Calcium.—J. Stingl,[‡‡] "On the Valuation of Burned Lime."

Magnesium.—A. Classen[§§] determines magnesium in the following manner: The solution, whose volume should be about 25 cc., is treated with a saturated solution of ammonium oxalate until whatever precipitate is produced is redissolved. It is then heated to boiling; and an equal volume of 80 per cent. acetic acid added; the boiling is continued for some minutes with constant agitation; after which the whole is allowed to stand six hours at a temperature of about 50°. The precipitate is separated by filtration, washed with a solution consisting of equal volumes of strong acetic acid and alcohol, and finally converted into oxide by heating in a platinum crucible. If it is desired to separate magnesium from the alkalies by this method, it is necessary to make the solution more dilute (50 cc. instead of 25), and to employ a less concentrated solution of ammonium oxalate (1 part of the salt dissolved in 25 parts of water), also to add a quantity of alcohol equal to about one-third of the volume of the liquid.

In order to determine magnesium volumetrically, H. Precht[||||] treats the solution containing it with a measured quantity of a standard solution of caustic potassa, dilutes to a known volume, allows the magnesium hydroxide to subside, and estimates the excess of the alkali in a measured portion of the liquid by means of a standard acid.

Zinc.—F. Selmi,[¶¶] "On the Conduct of Zinc towards Phosphorus, Phosphide of Hydrogen, Sulphide of Hydrogen and Iron Salts."

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[*] Z. an. Ch. 18, 559.

[†] Ber. d. d. ch. Ges. 1879, 1547.

[‡] Ber. 1879, 2376.

[§] Dingler's Journal, 231, 331.

[||] Z. an. Ch. 18, 560.

[¶] Z. an. Ch. 18, 509.

[**] Z. an. Ch. 18, 462.

[††] Z. an. Ch. 18, 563.

[‡‡] Z. an. Ch. 18, 501.

[§§] Z. an. Ch. 18, 373.

[||||] Z. an. Ch. 18, 438.

[¶¶] Z. an. Ch. 18, 471.

J. B. Schober[*] determines zinc volumetrically by adding to its solution a measured quantity of a standard solution of an alkaline sulphide and, then, of silver nitrate; after which the excess of silver is estimated by Volhard's method.

A. Classen[†] determines zinc by precipitation as oxalate in precisely the same manner as magnesium, except that neutral potassium oxalate is used instead of the ammonium salt. The method[‡] may be employed for the separation of zinc from iron and aluminium.

Copper.—By this method[§] copper, also, may be determined and separated from iron aluminium.

W. Ohl,[||] "On the Electrolytic Determination of Copper, etc."

Nickel.—According to A. Classen[¶] the oxalate method is also applicable to the determination of nickel and its separation from iron and aluminium.

W. Ohl,[**] "The Electrolytic Determination of Nickel, etc."

E. Donath[††] bases on the different conduct of nickel and cobalt towards iodine a method of determining the two when they occur together. The solution containing the metals is divided into two equal portions. One is treated with caustic potassa and bromine; the other, with caustic potassa and iodine. In the first case both nickel and cobalt are converted into sesquioxides; in the second, only the cobalt. The precipitates are finally treated with hydrochloric acid and the quantity of chlorine liberated by each determined by the iodine method.

P. Dirvell[‡‡] separates the two metals by adding to their solution a mixture of a solution of acid carbonate of ammonium and of a phosphate, and gently warming. Cobalt is precipitated but not nickel.

Cobalt.—W. Ohl,[§§] "On the Electrolytic Determination of Cobalt, etc."

Cobalt, according to Classen,[||||] can also be quantitatively precipitated and separated from iron and aluminium by means of oxalate of potassium and acetic acid.

Iron.—R. Schœffel,[¶¶] "The Determination of Chromium and Tungsten in Steel and Iron Alloys."

J. Jewett,[***] "Influence of Acetic Acid on the Separation of Iron as Basic Acetate from Manganese, Zinc, Cobalt and Nickel."

P. Derome[†††] states that phosphoric acid may be separated from the oxides of iron and aluminium by strongly heating the material, mixed with five or six times its weight of dried sulphate of sodium, eight or ten minutes before the blast lamp.

T. Twynam,[‡‡‡] "Method for the Estimation of the Oxide of Iron and Alumina in Commercial Phosphates."

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[*] Z. an. Ch. 18, 467.

[†] Z. an. Ch. 18, 189.

[‡] Z. an. Ch. 18, 381.

[§] Z. an. Ch. 18, 388.

[||] Z. an. Ch. 18, 523.

[¶] Z. an. Ch. 18, 189, 379, 386.

[**] Z. an. Ch. 18, 522.

[††] Ber. d. d. chem. Ges. 1879, 1868.

[‡‡] Comptes rendus, 89, 903.

[§§] Z. an. Ch. 18, 523.

[||||] Z. an. Ch. 18, 189, 379, 384.

[¶¶] Ber. d. d. ch. Ges. 1879, 1863.

[***] This Journal, 1, 251.

[†††] Comptes rendus, 89, 952.

[‡‡‡] Chem. News, 40, 203.

Manganese.—F. Beilstein and L. Jawein[*] propose two methods for the direct separation of manganese and iron. By the first, the metals are converted into soluble potassium-mangano- and ferrocyanides, and the manganese then precipitated by means of iodine. By the second they are dissolved in strong nitric acid and chlorate of potassium added. The manganese is completely precipitated, but always contains a small quantity of iron.

J. Volhard[†] has published an investigation of unusual interest and importance on the separation and determination of manganese. He finds that the volumetric method of determining manganese by permanganate of potassium yields unsatisfactory results when it is employed as directed by Guyard, its originator, and others. If, however, some salt of an unoxidizable metal, other than potassium or sodium, is added to the solution in which the determination is to be made, the method yields results which are quite accurate.

The reaction, so far as the two manganese compounds are concerned, is as follows: $3MnO + Mn_2O_7 = 5MnO_2$. The neutral and dilute solution of manganese is placed in a long necked flask, acidified with three or four drops of pure nitric acid and about one gram of zinc sulphate added. The solution is then heated to boiling. After which it is treated with permanganate as long as the color disappears. In order to facilitate the subsidence of the precipitate the contents of the flask are vigorously agitated and possibly reheated. The presence of ferric salts in any considerable quantity interferes with the success of the method. These however may be completely removed by addition of oxide of zinc. The author recommends that the value of permanganate solutions to be used in volumetric work be determined by means of a pure manganese salt.

F. Stolba[‡] recommends the use of oxalate of lead in standardizing permanganate solutions.

Chromium.—T. Wilm[§] finds that chromium oxide, which has been obtained by precipitation of the hydroxide with ammonia, undergoes oxidation when ignited in contact with the air. This oxidation he supposes to be due to the presence of calcium derived from the ammonia.

Lead.—F. Salomon,[||] "The Determination of the Acid in Sugar of Lead and Lead Vinegar."

Platinum.—L. L. de Koninck,[¶] "On the Destructibility of Platinum by Fusing Alkaline Carbonates."

Hydrocarbons.—The Testing of Petroleum.[**]

Hydroxyl Derivatives of Hydrocarbons.—P. Waage,[††] "Studies on the Ebullioscope."

Organic Acids, Esters, Salts and their Derivatives.—R. Andreasch[‡‡] finds that, when a salt of thioglycolic acid is treated with

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[*] Ber. d. d. ch. Ges. 1879, 1528.

[†] Liebig's Ann. 198, 318.

[‡] Z. an. Ch. 18, 600.

[§] Ber. d. d.ch. Ges. 1879, 2223.

[||] Dingler's Journal, 234, 222.

[¶] Z. an. Ch. 18, 569.

[**] Ch. News, 40, 305; Ber. d. d. ch. Ges. 1879, 2184; Dingler's Journal, 234, 52.

[††] Z. an. Ch. 18, 417.

[‡‡] Z. an. Ch. 18, 601.

a ferric compound and a little ammonia, a dark purple-violet color is produced. On standing the color diminishes, but can be restored by agitating the liquid with air. As a reagent for detecting the presence of ferric compounds this substance exceeds sulphocyanide of potassium in sensitiveness.

L. Claisen,[*] " A Reaction for Phenylglyoxylic Acid."

B. J. Grosjean,[†] "On the Determination of Tartaric Acid in Lees and inferior Argol, with some Remarks on Filtration and Precipitation."

H. Schiff,[‡] " Determination of Acetyle by Means of Magnesia."

E. Meissl,[§] " Investigations on the Adulteration of Commercial Melted Butter."

F. Tschaplowitz,[||] " Apparatus for the Determination of Fats."

F. Soxlet,[¶] " The Gravimetric Determination of Milk-Fat."

J. Wolff,[**] " Separation of Fats and Soaps."

O. Brenken,[††] " On the Investigation of Mineral Lubricating Oils."

O. Cailletet,[‡‡] " Examination of Olive Oil for Copper."

Carbohydrates.—W. Müller,[§§] " Detection of Grape Sugar by Means of Acetate of Copper."

F. W. Pavy,[||||] " Pavy's Method of Estimating Glucose."

J. Steiner,[¶¶] " The Ammoniacal Copper-Test and its Application"—Pavy's method.

P. De P. Ricketts,[***] "A Method for the Detection of artificial or dextro Glucose in Cane Sugar, and the exact Determination of Cane Sugar by the Polariscope."

P. Casamajor,[†††] " On the Influence of Variations of Temperature on the Deviation of Polarized Light by Solutions of Inverted Sugar."

P. Casamajor,[‡‡‡] " New Process for the rapid Estimation of Pure Sugar in Raw and Refined Commercial Sugars."

Abeles,[§§§] " The Sugar contained by Normal Urine."

J. Seegen,[||||||] " On the Supposed Occurrence of Sugar in Normal Urine."

Urea.—C. Méhu[¶¶¶] states that when sugar is added to a solution of urea, nearly all the nitrogen is liberated on treatment with hypobromite of sodium.

G. Esbach,[****] however, finds that the larger volume of gas obtained when sugar is present is due to a decomposition of the sugar by the hypobromite.

Méhu[††††] reaffirms the correctness of his original observations.

E. Drechsel and J. Haycraft,[‡‡‡‡] Separation of Urea from Dog's Blood by Dialysis and Subsequent Determination of the same.

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[*] Ber. d. d. ch. Ges. 1879, 1505.

[†] Jr. Ch. Soc. 1879, 341.

[‡] Ber. d. d. ch. Ges. 1879, 1531.

[§] Dingler's Journal, 233, 229.

[||] Z. an. Ch. 18, 441.

[¶] Dingler's Journal, 232, 461.

[**] Z. an. Ch. 18, 570.

[††] Z. an. Ch. 18, 546.

[‡‡] Z. an. Ch. 18, 628.

[§§] Z. an. Ch. 18, 600.

[||||] Chem. News, 39, 249.

[¶¶] Ch. News, 40, 139.

[***] Jr. Am. Ch. Soc. 1, 2.

[†††] Jr. Am. Ch. Soc. 1, 26.

[‡‡‡] Jr. Am. Ch. Soc. 1, 205.

[§§§] Ber. d. d. ch. Ges. 1879, 1704.

[||||||] Ber. d. d. ch. Ges. 1879, 1705.

[¶¶¶] Comptes rendus, 89, 175.

[****] Comptes rendus, 89, 417.

[††††] Comptes rendus 89, 486, 616.

[‡‡‡‡] Jr. prak. Ch. 19, 334.

Alkaloids.—J. Tattersall,[*] "A New Test for Papaverine."

A Poehl,[†] On Distinguishing Atropin from Daturine.

Glenard,[‡] On Distinguishing Quinine from Cinchonine.

H. Ranke,[§] Experiments on the Detection of Strychnine in the decomposing Cadaver.

F. Selmi,[||] On the Alkaloids of the Cadaver.

A. Loesch,[¶] "On the quantitative Determination of the Alkaloids of Plants."

Miscellaneous.—F. Fischer,[**] "On the Investigation of Atmospheric Air."

W. Van Slooten,[††] "Analysis of Air."

Ira Remsen,[‡‡] "Organic Matter in the Air."

G. Aarland,[§§] "Analysis of Ores and Furnace Products."

A. Terreil,[||||] "Analysis of some metallic Fragments from Peruvian Graves."

F. Mauro,[¶¶] "An Analysis of Spinel."

Maumené,[***] "On the Composition of Slate."

A. Smethan,[†††] "Composition of a Boiler Incrustation."

D. Playfair,[‡‡‡] "On the Detection of some rare Metals in Pyrites Flue-Dust."

C. Zimmermann,[§§§] "On the Separation of the heavy Metals of the Sulphide of Ammonium Group."

B. Corenwinder and G. Contamine,[||||||] "A new Method of Analyzing with Precision the Potashes of Commerce."

E. F. Smith,[¶¶¶] "New Results in Electrolysis."

C. J. H. Warden,[****] "Analysis of Poppy Petal Ash."

S. F. Peckham,[††††] "On the Composition of the Ashes of Wheat-Bran burned under a Steam Boiler."

L. Ricciardi,[‡‡‡‡] "Analysis of Tobacco."

G. Stein,[§§§§] "On the Analysis of Turkey-Red."

A. W. Blythe,[||||||||] "The Composition of Cow's Milk in Health and Disease."

W. H. Watson,[¶¶¶¶] "On the Detection of Milk Adulteration."

F. Becker,[*****] "Examination of Beeswax."

M. Buchner,[†††††] "On the Adulteration of Beeswax."

J. M. Eder,[‡‡‡‡‡] "The Examination and the Properties of Chinese Tea."

C. Husson,[§§§§§] "A Study of Tea, Coffee and Chiccory."

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[*] Chem. News 40, 126

[†] Z. an. Ch. 18, 628.

[‡] Z. an. Ch. 18, 629.

[§] Z. an. Ch. 18, 635.

Z. an. Ch. 18, 506.

[¶] Chem. Centralblatt 1879, 812, 826.

[**] Dingler's Journal 234, 46.

[††] Jr. Am. Ch. Soc. 1, 263.

[‡‡] Bull. National Board of Health, Jan. 31, 1880.

[§§] Ber. d. d. ch. Ges. 1879, 270.

Bull. de la Soc. chim. 31, 151.

[¶¶] Ber. d. d. ch. Ges. 1879, 685.

[***] Comptes rendus, 89, 423.

[†††] Chem. News 39, 236.

[‡‡‡] Chem. News 39, 245.

[§§§] Lieb. Ann. 199, 1.

Comptes rendus, 89, 907.

[¶¶¶] This Journal 1, 329.

[****] Chem. News 39, 27.

[††††] Chem. News 39, 244.

[‡‡‡‡] Ber. d. d. ch. Ges. 1879, 683.

[§§§§] Ber. d. d. ch. Ges. 1879, 1174.

Jr. Chem. Soc. 1879, 530.

[¶¶¶¶] Ch. News 40, 102.

[*****] Ber. d. d. ch. Ges. 1879, 2099.

[†††††] Dingler's Journal 231, 272.

[‡‡‡‡‡] Dingler's Journal 231, 445, 526.

[§§§§§] Ann. de Chim. [5] 16, 419.

Means of Detecting the Adulteration of Saffron.[*]

D. Lindo,[†] "Examination of Caoutchouc Goods."

J. M. Kostersitz and F. Hess,[‡] "On the Valuation of Explosives."

D. Vitali and H. Schiff,[§] "Examination of old Blood."

H. R. Proctor,[||] "Determination of the free Acid in Tan Liquors."

A. Houzeau,[¶] "On Gravivolumetry."

F. Salomon,[**] "Quantitative Determination of Colored Acids."

G. Williams,[††] "On the new Substitute for Litmus."

A. H. Allen,[‡‡] "Normal Solutions."

F. A. Gooch,[§§] "On a new Method for the Separation and Subsequent Treatment of Precipitates in Chemical Analyses."

K. Kraut,[||||] "On Filter-paper and Filtration."

R. Popper,[¶¶] "Quantitative Determination of Precipitates without Filtering, Washing or Drying the same."

J. H. Poynting,[***] "On the Estimation of small Excesses of Weight by the Balance from the time of Vibration and the Angular Deflection of the Beam."

H. N. Morse.

NOTES.

Synthesis of Formic Acid.

V. Merz and J. Tibiriça sum up the results of an elaborate investigation on the action of carbon monoxide on alkalies with these statements:

Carbon monoxide is absorbed by caustic alkalies at about 200°, and a salt of formic acid is produced.

In order to saturate caustic soda as thoroughly as possible, it should be used in the form of soda-lime; this should be very porous, the gas should be moist, and the temperature not above 220°.

As the absorption of carbon monoxide takes place rapidly when the proper precautions are observed, formic acid, or formates, may best be prepared on the large scale from inorganic material.

According to the information furnished in Wagner's Jahresbericht, formic acid appears to be used principally in the manufacture of certain esters. But it would now be interesting to de-

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[*] Chem. News, 39, 35

[†] Chem. News 39, 99.

[‡] Z. an. Ch. 18, 623.

[§] Ber. d. d. ch. Ges. 1879, 684.

[||] Chem. News 39, 246.

[¶] Comptes rendus 88, 747.

[**] Dingler's Journal 234, 317.

[††] Chem. News 39, 98.

[‡‡] Chem. News 40, 239.

[§§] This Journal 1, 317.

[||||] Z. an. Ch. 18, 543.

[¶¶] Z. an. Ch. 18, 14.

[***] Chem. News 39, 45.

termine how far this acid may be used for technical purposes in place of acetic acid, and also as a reducing agent. It should further be remarked that according to Jodin* free formic acid is an antiseptic, and under some conditions is superior to phenol in this respect.—(*Ber. d. deutsch. chem. Gesell.* 13, 23.)

The Valence of Boron.

Nearly all the known compounds of boron can be explained on the assumption that the element is trivalent. Two compounds have been described, however, which indicate that boron may, under some circumstances, play the part of a quinquivalent element. These are an ester prepared by Frankland, to which he gives the formula $B_2(C_2H_5)(OC_2H_5)_3$, and an oxychloride $BOCl_3$ prepared by C. Councler. A. MICHAELIS and P. BECKER have now shown that, if a phenyl derivative of the trichloride of boron be first prepared, according to the following equation:

$$2BCl_3 + Hg(C_6H_5)_2 = 2C_6H_5BCl_2 + HgCl_2,$$

this substance readily takes up chlorine. A product is formed which is called *phenylboron tetrachloride*, $C_6H_5BCl_4$. This corresponds to similar derivatives obtained from phosphorus and arsenic, and makes it very probable that boron may be either trivalent or quinquivalent.—(*Ber. d. deutsch. chem. Gesell.* 13, 58.)

Artificial Alkaloids.

A. LADENBURG continues his interesting studies of the alkaloids. He finds that the atropine obtained by him in treating the tropate of tropine with dilute hydrochloric acid is identical with natural atropine. He has, further, treated other salts of tropine in the same way, and thus obtained representatives of a class of artificial alkaloids to which he gives the generic name *tropeïnes*. The three substances of this class described are made from the salicylate, oxytoluate and phthalate of tropine. Oxytolutropeïne acts upon the human pupil almost as energetically as atropine. It has been used extensively in the ophthalmological clinic, and the conclusion drawn from the experiments thus far performed is that in many cases it is to be preferred to atropine.—(*Ber. d. deutsch. chem. Gesell.* 13, 104.)

On the new Hydrogen Lines and the Dissociation of Calcium.

H. W. VOGEL has photographed the spectrum of pure hydrogen, evolved by electrolysis, and finds certain new lines, among which the most striking is one which is almost coincident with the line H′ (Frauenhofer) usually attributed to calcium. This is called the *fifth principal hydrogen line*. The discovery of this new line of hydrogen is of interest in connection with Lockyer's supposition

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* Wagner, Jahresbericht, 1866, 287, and Zeitschrift f. Chem. 1866, 95.

that calcium is dissociated at a very high temperature. Lockyer has suggested that when calcium is dissociated it is broken up into two bodies, X and Y, and that the first H line belongs to one of these and the second line to the other. Huggins has shown that of the two thick H-lines of the solar spectrum only the first is present in the spectra of Sirius and Vega. According to Lockyer, this isolated line is due to the presence of one of the components of dissociated calcium. Vogel, on the other hand, believes that it is the fifth hydrogen line, and has consequently no connection with calcium. Lockyer has, further, called attention to an observation made by Young, according to which the H′-line was seen to be injected into the chromosphere 25 times and the H″-line 50 times. The appearance of the H′-line alone is explained on the supposition that it is due to dissociated calcium. But Vogel believes that the H′-line seen alone was the fifth hydrogen line.—(*Ber. d. deutsch. chem. Gesell.* 13, 274.)

Chlorine, Bromine and Iodine at High Temperatures.

VICTOR MEYER* and J. M. CRAFTS† have shown that when pure chlorine is heated to yellow heat its density is not changed, as it is when produced in the nascent state. It seems quite impossible, at present, to furnish a satisfactory explanation for this difference between free and nascent chlorine.

Meyer has communicated some details in regard to the density of iodine at high temperatures. He shows that at 800° there is a marked decrease in the density, and, from about 1027 to 1567°, it remains unchanged and is exactly equal to the value calculated for $\frac{2}{3}Cl_2$.

Crafts,‡ however, finds that the density of iodine vapor does not remain unchanged after the value corresponding to the formula $\frac{2}{3}Cl_2$ is reached, but that there is a still further decrease.

THE chair of chemistry in the newly established Agricultural College of Berlin, is to be filled by PROF. H. LANDOLT, of Aix-la-Chapelle, well-known by his exhaustive studies on the relations between the optical properties of bodies and their chemical constitution. His wide experience in saccharimetry has likewise led to his simultaneous appointment as director of the chemical laboratory established at Berlin by the German *Verein für Rübenzucker-Industrie.* Prof. Landolt is succeeded in the Polytechnic of Aix-la-Chapelle by PROF. A. CLASSEN, who has recently published two favorably received laboratory manuals on Qualitative and Quantitative Analysis.—(*Nature.*)

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* Berichte d. deutsch. chem. Gesell. 13, 399.

† Compt. rend. 90, 183.

‡ Compt. rend. 90, 690.

IT is proposed to commemorate, by a permanent memorial, the distinguished services rendered to science and education by DR. THOMAS ANDREWS, during the thirty years that he was occupant of the chair of chemistry in the Queen's College, Belfast.

THE French chemist, SAINTE-CLAIRE DEVILLE, has resigned the professorship at the École Normale of Paris which he has held for twenty-nine years. He is succeeded by L. TROOST, who has long been well-known for his careful investigations in the field of inorganic chemistry.

M. ZININ, the well-known Russian chemist, recently died at St. Petersburg. One of his chief discoveries was the conversion of nitro- into amido-compounds. One of the first substances made in this way was aniline.

PAUL MENDELSSOHN BARTHOLDY, a son of the composer, and himself a chemist well-known in connection with chemical industry, recently died in Berlin. He was a member of the firm of Martius & Mendelssohn of Berlin, manufacturers of aniline and aniline colors.

PROF. JAMES M. CRAFTS has recently been awarded a prize by the French Academy of Sciences for his researches in the field of organic chemistry.

PROF. A. R. LEDOUX, Director of the North Carolina Agricultural Experiment Station, has resigned.

PROF. GEORGE A. SYMTH, of the University of Vermont, has left his professorship and engaged in work in connection with sanitary chemistry at Newport.

RECENT PUBLICATIONS RELATING TO CHEMISTRY.

I. - ENGLISH.

BLOXAM, C. L. Chemistry, Inorganic and Organic, with Experiments. 4th Edition. London: Churchill. 16s.

CLOWES, F. Elementary Treatise on Practical Chemistry and Qualitative Analysis. 3d Edition. London: Churchill. 7s. 6d.

EAGLE, J. A Note-book of Solubilities, arranged chiefly for the use of Prescribers and Dispensers. London: Lewis. 2s. 6d.

Frankland, E. Water Analysis for Sanitary Purposes. With Hints for the Interpretation of Results. London: Van Voorst. 5s.

Jarmain, G. Systematic Course of Qualitative Analysis, arranged in Tables. 4th Edition. London: Longmans. 1s. 6d.

Percy, J. Metallurgy: the Art of Extracting Metals from the Ores. Silver and Gold, Part I. London: Murray. 30s.

Robinson, H. Sewage Disposal. London: Spons. 4s.

Tilden, W. A. Practical Chemistry: the Principles of Inorganic Analysis. London: Longmans. 1s. 6d.

II.—French.

Girardin, J. Leçons de chimie élémentaire appliquée aux arts industriels. 6^{e} Ed. Supplement aux 5 vol. Masson. 5fr.

III.—German.

Artus, F. W. Grundzüge der Chemie in ihrer Anwendung auf das praktische Leben. Wien: Hartleben. M. 6.00.

Dammer, O. Kurzes chemisches Handwörterbuch. Berlin: Oppenheim. M. 17.00.

Eppinger, O. Ueber die Einwirkung des Aethyl- und Diaethylamins auf Aceton. Halle-Wittenberg.

Fischer. Die chemische Technologie des Wassers. Braunschweig: Vieweg und Sohn. M. 11.60.

Hempel. Neue Methode zur Analyse der Gase. Braunschweig: Vieweg und Sohn. M. 5.00.

Jacobsen. Die chemische Industrie. 3 Jahrg. Berlin: Springer. M. 20.

Jahresbericht über die Fortschritte auf dem Gesammtgebiete der Agricultur-Chemie. Begründet v. R. Hoffmann, fortgeführt v. A. Hilger. Das Jahr 1878. Berlin: Springer. M. 22.00.

Lorscheid, J. Lehrbuch der anorganischen Chemie nach den neuesten Ansichten der Wissenschaft. 8 Aufl. Freiburg: Herder. M. 4.40.

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ON THE DETERMINATION OF ALBUMINOIDS IN HAY AND COARSE FODDERS.

BY H. P. ARMSBY.

In the analysis of feeding-stuffs and of vegetable products in general, the albuminoids are commonly determined by multiplying the percentage of nitrogen found by analysis by 6.25, it being assumed that the albuminoids contain 16 per cent. of nitrogen, and that no other nitrogenous bodies are present. Recent investigations have, however, shown that the latter assumption in particular is frequently far from being true, and that many feeding-stuffs contain relatively large amounts of non-albuminoid nitrogenous matters, consisting chiefly of amides. These bodies have been found to be especially abundant in beets and other roots, in potatoes, and in grass and hay, while the seeds of plants appear to be comparatively free from them.

In view of the probable inferior nutritive value of these amides and other bodies, which we shall here designate for convenience as *non-albuminoids*, it becomes desirable, in the analysis of a feeding-stuff, to be able to separate them from the albuminoids and to determine their amount. Much the same difficulties which stand in the way of a direct determination of the albuminoids prevent a direct determination of the non-albuminoids as well; but, on the other hand, a more or less perfect separation of the albuminoid and non-albuminoid *nitrogen* may be made without special difficulty. Several processes have been proposed to effect this, all of which assume as their starting point that the non-albuminoids are soluble in water or acid liquids. Now, while this is true of all the bodies of this class known to exist in feeding-stuffs, and while it is very probably correct, it should be borne in mind that it is not proved. There is no reason in the nature of things why there should not be an insoluble amide, for example, as well as an insoluble albuminoid. If there be such, however, we have no means of ascertaining the fact at present, and can only adopt provisionally the assumption just mentioned as a working hypothesis.

Taking this as a starting point, the several methods proceed in general as follows:

The substance to be examined is first boiled with water slightly acidified with some organic acid or with water alone; this process dissolves out the non-albuminoids (with the reservation made above), while most or all of the albuminoids are either not dissolved at all or are coagulated by boiling. Some substance is then added to the liquid which will precipitate any dissolved albuminoids which it may still contain, without affecting the non-albuminoids, the mass is filtered, and a nitrogen determination made either in the insoluble matters or in the filtrate.

In the first case we get directly the albuminoid nitrogen, in the second case it is obtained by subtracting the nitrogen of the filtrate from the total nitrogen of the substance. The several methods differ essentially only in the precipitant employed. Church[*] recommends a four per cent. solution of carbolic acid, Sestini[†] uses lead acetate, Dehmel[‡] has obtained concordant results by the use of copper sulphate as proposed by Ritthausen, and E. Schulze[§] proposes the use of ferric acetate as recommended by Hoppe-Seyler. More or less uncertainty, however, is involved in all these methods, since, although the precipitants employed doubtless remove all the albuminoids from solution, we are largely ignorant of the nature of the amides and other bodies extracted by water, and run the risk of precipitating them from the solution by means of the reagents intended to effect the removal of albuminoids.

These considerations led the writer to experiment on the possibility of dispensing with precipitants altogether, and the results on

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[*] Laboratory Guide, 4th ed., 209.

[†] Landw. Versuchs-Stationen, 23, 305.

[‡] Ibid. 24, 214.

[§] Landw. Jahrbücher, 6, 160.

hay have been so satisfactory that he feels induced to describe the method adopted.

Comparative trials were first made on three samples of hay which had previously been analyzed, carbolic acid, lead acetate, and cupric sulphate being all used as precipitants.

The experiments with carbolic acid and lead acetate were made according to the directions of Church and Sestini respectively. In the experiments with cupric sulphate the substance was boiled for an hour with water, then 10 c. c. of a ten per cent. solution of cupric sulphate was added, the boiling continued for a few minutes, the mass then filtered, and the nitrogen of the insoluble residue determined.

In the trials with water the substance was simply boiled for an hour with water slightly acidified with lactic acid, filtered, and treated as in the other methods. In each trial 0.5 gram of hay was used, and each result is the mean of two accordant determinations.

	No. 1.	No. 2.	No. 3.
Water,	11.31 per cent.	10.75 per cent.	11.19 per cent.
Total nitrogen,	1.30 "	0.81 "	2.39 "
Albuminoid nitrogen,			
By Church's method,	1.22 "	0.68 "	1.93 "
By Sestini's "	1.18 "	0.62 "	1.83 "
By copper sulphate method,	1.22 "	0.69 "	1.89 "
By extraction with water,	1.11 "	0.61 "	1.92 "
Average,	1.18 "	0.65 "	1.89 "
Non-Albuminoid nitrogen,	0.12 "	0.16 "	0.50 "

In all cases (except in Church's method, where it is impossible)* the filtrate was tested for albuminoids by Millon's reagent and found to be free from them.

These results show: first, that these samples of hay contained a considerable proportion of non-albuminoid nitrogen; second, that all four of the methods used for the determination of albuminoid nitrogen gave practically the same result, and consequently the use of any reagent to precipitate dissolved albuminoids was unnecessary in these cases.

In addition to these experiments, the albuminoid nitrogen in

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* In endeavoring to test the filtrate obtained by Church's method it was found that carbolic acid gives with Millon's reagent a color which, in very dilute solutions, simulates closely that produced by albuminoids, except that it appears, after a time, in the cold. This fact does not appear to have been previously noticed.

twenty-one samples of hay and stover has been determined by treatment with water in the manner described above, and in no case could albuminoids be detected in the filtrate, so that we are justified in concluding that in the analysis of hay a separation of the albuminoid and non-albuminoid nitrogen may be effected most simply by means of boiling water. That this method is preferable to the use of precipitants is obvious. Whether it is applicable to all feeding-stuffs is perhaps doubtful. Some experiments on rye-bran and malt sprouts seem to indicate that it is not, but to hay at least it is perfectly applicable, and by its aid it is a very simple matter to determine the amount of albuminoid nitrogen present, and by multiplication by 6¼ to calculate approximately the amount of albuminoids.

To ascertain whether the method of extraction adopted brought all the non-albuminoids into solution, the following trials were made on a sample of clover hay containing 2.41 per cent. of nitrogen. One-half gram of the hay was boiled with slightly acidulated water for 45 minutes, filtered through an asbestos filter, and the insoluble residue burned with soda-lime. A second portion of one-half gram was boiled with acidulated water for 30 minutes, filtered through asbestos, the residue returned to the dish, boiled 30 minutes longer with acidulated water, and then filtered and burned as before. A third portion was submitted to three extractions in the same manner. Each experiment was made in duplicate, and the following results obtained for albuminoid nitrogen:

One extraction,	1.85 and	1.89	per cent.
Two extractions,	1.78	1.87	"
Three extractions,	1.82	1.84	"

Evidently one extraction removed all the soluble nitrogen.

A diffusion experiment was also made, to see if there were any indications of the presence of soluble albuminoids in the filtrate. Twenty grams of the hay were boiled for forty-five minutes with acidulated water, filtered, and washed with hot water. The filtrate was introduced into a parchment paper dialyser and allowed to diffuse into a constantly renewed volume of water for nearly two days. It was then diluted to 1000 c. c., and two portions of 50 c. c. evaporated to dryness in Hofmeister glass capsules and burned with soda lime. Calculated on the original substance, the results were 0.08 per cent. and 0.10 per cent. of nitrogen, or an average of 0.09

per cent., as the amount of indiffusible nitrogen extracted by this process.

It would thus appear that the method of extraction with boiling water effects a very satisfactory separation of the albuminoid and non-albuminoid nitrogen of hay. It has the advantage of simplicity, and while its results are, like all the results of fodder analysis, sufficiently crude, they are no more so than those obtained by the use of more complicated methods, and are an advance on those reached by simply determining the total nitrogen.

CONNECTICUT AGRICULTURAL EXPERIMENT STATION, March, 1880.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

NO. III.

PARACHLORBENZYL COMPOUNDS.*

BY C. LORING JACKSON AND ALFRED W. FIELD.

Parachlorbenzylchloride, $C_6H_4ClCH_2Cl$. In beginning these researches, we had no idea that it would be necessary to investigate this substance, as, since its discovery by Beilstein and Geitner,† it had been prepared and studied by a great number of chemists, and had served as the starting-point for the preparation of all the parachlorbenzyl compounds known. But, on looking into the subject more carefully, we found that it had been made invariably from the product of the chloriring of toluol in the cold, which Hübner and Majert‡ have proved, by their work on the sulpho-acids, is a mixture of ortho- and parachlortoluol; while, more recently, Oscar Emmerling§ has shown that the product from ox-

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* Proceedings American Academy of Arts and Sciences. Communicated by the Authors.

† Beilstein and Geitner, Zeitschr. der Chem. 1866, 307; also 17.

‡ Hubner and Majert, Ber. d. ch. G. 6, 790.

§ O. Emmerling, Ber. d. ch. G. 8, 880.

idizing it with potassic permanganate contains more ortho- than parachlorbenzoic acid. The parachlorbenzylchloride of previous chemists, therefore, must have been contaminated with a larger or smaller amount of the ortho compound, which escaped detection, because the method used by them to test the purity of their preparations consisted in oxidizing with potassic dichromate and sulphuric acid, and, as this destroys the ortho modification completely, a pure parachlorbenzoic acid was the only product. This oversight is not surprising when it is borne in mind that the more important of these papers appeared in 1866, when the nature of aromatic isomeres was very imperfectly understood.

For the reason given above, we determined to prepare the parachlorbenzylchloride from perfectly pure parachlortoluol, and hoped that it might be a solid, instead of the oily liquid described by our predecessors; indeed, it seemed hard to believe that it could be a liquid, as the parachlortoluol melts at 6½° (Hübner and Majert), and we have found that the introduction of bromine into the side-chain raised the melting-point to 48½°.

Preparation. Parachlortoluol was made from pure paratoluidine by treatment with hydrochloric acid and potassic nitrite, according to a modification of the method of Hübner and Majert* described in connection with parachlorbenzylbromide in the first paper† of this series. The 31 grams that we obtained distilled over completely between 160° and 161°, and froze between 4° and 5° in white plates looking exactly like parabromtoluol, which melted from 7° to 7½°. These results agree essentially with those of Hübner and Majert,* who found the boiling-point 160½°, the freezing-point a little above 0°, and the melting-point 6½°. To convert this into parachlorbenzylchloride, a stream of chlorine was passed into it while it stood in a paraffine-bath heated to 166°: when the increase in weight showed that somewhat more than the calculated amount of chlorine had been taken up (the 27 grams of parachlortoluol used had become 35 grams instead of 34.3 grams,) the chlorine was stopped, and the product put in a freezing mixture of ice and salt, where it partially solidified in white needles, which were drained on the filter-pump, and recrystallized from alcohol. The yield was very small, and all attempts to get more from the mother-liquors were fruitless. The following analyses of the substance dried *in vacuo* show that it is the expected parachlorbenzylchloride.

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* Hubner and Majert, Ber. d. ch. G. 6, 794.

† This Journal, 1, 100.

0.6760 gram of substance gave 1.2930 gram of CO_2 and 0.2458 gram of H_2O.*

0.2755 of substance gave, by Klobukowski's† modification of Emil Kopp's method, 0.4946 gram AgCl.

	Calculated for $C_7H_6Cl_2$.	Found.
Carbon,	52.17	52.17
Hydrogen,	3.73	4.04
Chlorine,	44.10	44.41
	100.00	100.62

Properties. White lustrous prisms or needles, often more than 3 cm. long, with an agreeable aromatic odor and most violent action on the mucous membrane and tenderer parts of the skin; melting point, 29°; so volatile that a crystal exposed to the air disappears in a few hours; sublimes even at ordinary temperatures in needles; it is very little, if at all, soluble in water, but readily in warm, less so in cold, alcohol, very easily in ether, benzol, carbonic disulphide, and glacial acetic acid. That it is a chlorbenzyl compound was proved by boiling it for some time with water, in a flask with a return-cooler, when the parachlorbenzylalcohol and hydrochloric acid were formed. Boiled with a solution of potassic permanganate, it was easily oxidized, giving an acid which melts between 233° and 235° (O. Emmerling gives 234° as the melting-point of parachlorbenzoic acid); this acid boiled with water, in which the orthochlorbenzoic acid is much more soluble than the para, gave a solution which deposited crystals melting also at 233°–235°: as potassic permanganate oxidizes instead of destroying the ortho compounds, this proves that our parachlorbenzylchloride is perfectly free from isomeric impurities.

Having thus proved that the parachlorbenzylchloride used as a starting point for the preparation of derivatives by Beilstein, Kuhlberg, Neuhof, and others, really did contain the ortho compound, as we had previously inferred, we next proceeded to make some of these derivatives, and redetermine their properties. In this work, the more easily purified parachlorbenzylbromide was used instead of the chloride.

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* Combustion of these parachlorbenzyl compounds with plumbic chromate alone was found to yield good results much more easily than the more usual method of combustion in a stream of oxygen, and therefore was used in the analysis of all these substances.

† Klobukowski, Ber. dt. ch. G. 10, 290.

Parachlorbenzylalcohol, $C_6H_4ClCH_2OH$, was made by boiling the bromide (or chloride) with water in a flask with a return-cooler. The formation of hydrobromic (or hydrochloric) acid by this reaction was proved by testing the water, which had become acid, with argentic oxide, when argentic bromide (or chloride) was formed, and the acid reaction disappeared. The alcohol was made also from the acetate by boiling with water; sealing with aqueous ammonia, as recommended by Beilstein and Kuhlberg, being found in this case unnecessary; it was purified by crystallization from boiling water, dried *in vacuo*, and analyzed.

0.4517 gram of substance gave 0.9754 gram CO_2 and 0.2175 gram H_2O.

	Calculated for C_7H_6ClOH.	Found.
Carbon	58.94	58.89
Hydrogen	4.91	5.34

Properties. Beautiful pointed white ribbons usually one or two inches long, with a brilliant pearly lustre and characteristic smell, but no action on the mucous membrane or tenderer parts of the skin; melting point, 70½°; sublimes very easily in white needles, and can be purified in this way; evaporates slowly on exposure to the air, and distils in a current of steam; slightly soluble in cold, much more so in hot water, very easily in alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid. It is oxidized by a mixture of potassic dichromate and dilute sulphuric acid, giving parachlorbenzoic acid; melting-point, 233° (234° O. Emmerling.)

The chlorbenzylalcohol obtained by Beilstein and Kuhlberg* differs from the above only in melting at 66°.

Parachlorbenzylcyanide. The product of the reaction of alcoholic parachlorbenzylbromide and potassic cyanide, when precipitated by water, was a yellow oil, which showed no signs of solidifying in a mixture of ice and salt: after standing in an open watch-glass for three or more weeks, however, it did deposit crystals when put in a freezing-mixture, but in such small quantity that it was impossible to purify them thoroughly; and it did not seem worth while to spend the large amount of time and material necessary to get enough of them for complete study. The crystals, after sucking out the oil with filter-paper, proved to be good-sized colorless prisms; and, as one specimen of a twinned form like a quatrefoil was observed, there can be no doubt that the substance is analogous to the parabrom-

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* Beilstein and Kuhlberg, Ann. Chem. Pharm. 147, 339.

benzylcyanide, which will be described in a later paper of this series; its melting-point is 29°; and it is easily soluble in alcohol and ether, being left on evaporation of the solvent as an oil which crystallizes when stirred.

The yellow oil from which the crystals were obtained has also the nitrile smell, and is converted by heating to 100° in a sealed tube with hydrochloric acid, into parachloralphatoluylic acid: it must therefore be either the same substance as the crystals, prevented from solidifying by a small quantity of impurity, or the crystals may be a polymeric form of the oil. The cyanide was mentioned by Neuhof[*] as a dark oil, made by heating chlorbenzylchloride to 120°–130° in a sealed tube with potassic cyanide and alcohol; but no attempt was made to purify or analyze it. This heating in a sealed tube to 120°–130° is, as seen from the above, unnecessary.

Parachloralphatoluylic Acid, $C_6H_4ClCH_2COOH$, made by heating the nitrile to 100° in a sealed tube with fuming hydrochloric acid, or by boiling it with dilute sulphuric acid in a flask with a return-cooler, was purified by solution in ammonic hydrate, precipitation with sulphuric acid, and recrystallizing from boiling water. Its composition was established by an analysis of the silver salt.

Properties. White needles, often two centimetres long, sometimes thick and pointed, with a pleasant smell; melting-point, 103½°–104°; sublimes easily in little plates, and can be distilled, although not quickly, in a current of steam; somewhat soluble in cold, much more so in hot water, freely in alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid. Aqueous ammonia dissolves it readily, but the ammonic salt is decomposed, at least in part, by evaporation, the acid being set free.

A chloralphatoluylic acid has been already described as the para compound by Neuhof,[†] who made it, however, from chlorbenzylchloride; the melting-point was 60°, and it separated from its salts as an oil which soon solidified, otherwise it resembled our acid, except that it seems to have been much more soluble in water. Later, Radziszewski[‡] made a similar acid, melting at 68°, by chloriring alphatoluylic acid.

Argentic Parachloralphatoluylate, $C_6H_4ClCH_2COOAg$, fell as a white, curdy precipitate, upon adding argentic nitrate to a neutral solution of the ammonic salt of the acid. It was washed with water, dried at 100°, and analyzed.

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[*] Neuhof, Ann. Chem. Pharm. 147, 347.

[†] Ibid. 147, 347.

[‡] Radziszewski, Ber. d. ch. G. 2, 207

0.3410 gram of substance gave, precipitated from a nitric acid solution, with hydrochloric acid, 0.1788 gram of AgCl.

	Calculated for $C_8H_6ClO_2Ag$.	Found.
Silver	38.91	39.44

Properties. A white, curdy mass, consisting of clumps of silky microscopic needles, which blackens rapidly in direct sunlight, but only very slowly in diffused daylight, very slightly soluble in boiling water, almost insoluble in cold, freely soluble in dilute nitric acid and ammonic hydrate.

Neuhof obtained a similar salt, but describes it as more soluble in water than ours.

We did not succeed in getting a pure, well-defined *calcic salt*, although we tried to do so several times. By adding lime-water to the acid till the reaction was alkaline, removing the excess of lime by carbonic dioxide, and allowing the solution to evaporate spontaneously, arborescent groups of white needles were obtained. These lost 9.84 per cent. when dried at 100° ; 2 molecules of crystal water would give 8.68 per cent. ; 2½ molecules, 10.61 per cent. ; the loss, therefore, does not correspond to any probable amount of water of crystallization, and it seemed likely that something beside water was given off, as there was a slight sublimate on the upper watch-glass, and the substance had become somewhat brown, with a semifused look very unlike its original appearance. It, however, contained 10.36 per cent. of calcium, and may therefore have been the anhydrous salt which needs 10.55 per cent. Other experiments under different conditions gave no better results, and we therefore decided that the salt was not important enough to repay a thorough study, which would use up a great deal of time.

The *baric salt* was even less well defined than the calcic ; it was prepared in the same way, and appeared on evaporation of its solution over sulphuric acid as a colorless varnish, part of which changed on stirring into a radiated crystalline mass. This became white and opaque when treated with cold water, and when boiled with water gave an acid reaction and the smell of the acid. If the solution was evaporated on the water-bath instead of over sulphuric acid, a sticky gum was left. Neuhof's baric salt was similar to ours, and gave him an amount of barium corresponding to an acid salt. His calcic salt, on the other hand, contained one molecule of water, which it lost at 100°.

A solution of the acid in ammonic hydrate, from which the excess of ammonia has been driven off on the water-bath, gives the following characteristic reactions — bluish-green flocks with *cupric sulphate*, yellowish-brown with *ferric chloride*, and white with *plumbic acetate* or *mercurous nitrate*.

Parachlorbenzylsulphocyanate, $C_6H_4ClCH_2SCN$, made by boiling the bromide with an alcoholic solution of potassic sulphocyanate, was purified by freezing with snow and salt, sucking out the oil with filter paper, and recrystallization from alcohol with the help of a freezing mixture. It was dried *in vacuo* and analyzed.

0.1569 gram substance gave 0.1985 gram $BaSO_4$.

	Calculated for C_7H_6ClSCN.	Found.
Sulphur	17.43	17.38

Properties. White, flattened needles, often over an inch long, with a strong, disagreeable smell; melting-point, 17°; does not distil with steam, but seems to be slowly decomposed by it, a few brown drops with a smell like that of benzaldehyd passing over; mixes with alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid, but not with water.

This substance has not been made heretofore: it resembles the corresponding bromine compound very closely in everything but melting-point.

Parachlorbenzylamines.

These substances have been studied already by Berlin,* who prepared them by heating the chlorbenzylchloride with alcoholic ammonia for one week in the steam-bath. The product was worked up by a needlessly complex process, consisting, when stripped of its unnecessary steps, in separating one portion of the bases by conversion into their chlorides and crystallizing from alcohol, while in the remainder the tertiary amine was destroyed by distillation with bromine and water, and the bromides of the remaining amines separated by crystallization. The properties of the tertiary and primary amines, as described by him, are in no way peculiar; but he obtained four isomeric forms of the secondary amine, which were themselves undistinguishable yellow oils, but differed in the melting-points of their salts, as shown in the following table:—

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* Berlin, Ann. Chem. Pharm. 151, 137.

Name of Salt.	Melting Points.			
	α	β	γ	δ
Chloride	288°–289°	225°–228°	218°–220°	221°–222°
Bromide . . .	283°–290°	224	210°–212°	198°–199°
Iodide	. . . .	215	187°	216°–218°
Nitrate	. . . .	204°–205	193°	177°–179°

These salts also differed in solubility, the α modification being the least, the δ the most soluble: they were separated by crystallization of the bromides from water. These observations rendered a repetition of Berlin's work very interesting; but we did not follow the process given by him, as we have found a much more easy and simple method for the separation of the bases. Alcoholic ammonia acted very quickly, even in the cold, on parachlorbenzylbromide: the product from this or from the action in a sealed tube at 100° consisted of crystals either of the bromide of the tertiary amine or of the base itself, and of an alcoholic solution, which, filtered off and evaporated on the steam-bath, yielded the bromides of ammonium and of the primary and secondary amines with some free tertiary amine. This residue, after washing with water to remove the bromides of ammonium and the primary amine, was repeatedly crystallized from hot alcohol, until it was divided into slightly soluble scales of secondary bromide and needles of the free tertiary amine readily soluble in boiling alcohol.

Triparachlorbenzylamine, $(C_6H_4ClCH_2)_3N$, was freed from a trace of bromide by crystallizing from ether, dried *in vacuo*, and analyzed.

0.7096 gram of substance gave 1.6780 gram CO_2, and 0.3300 gram H_2O.

	Calculated for $(C_7H_6Cl)_3N$.	Found.
Carbon	64.78	64.49
Hydrogen	4.61	5.16

Properties. Bunches of white needles, when crystallized from alcohol; from ether it separates as an oil, which solidifies after some time in flattened prisms; it is also deposited from the action of cold alcoholic ammonia on parachlorbenzylbromide in short, thick, well-formed crystals, with rhombic faces; melting-point, 78½°; insoluble in water, very slightly soluble in cold, freely in hot alcohol, and in ether, benzol, and carbonic disulphide, less so in glacial acetic acid.

The *chloride* was obtained in an impure state when an alcoholic solution of the base was heated with strong hydrochloric acid; after standing 24 hours, the solution was allowed to evaporate spontaneously, when balls of radiated needles were left which melted at about 196°, were soluble in alcohol, ether, and glacial acetic acid, slightly in water, and insoluble, or nearly so, in carbonic disulphide and benzol; the alcoholic solution left a viscous mass, which changed into needles slowly. After drying *in vacuo*, it lost, in the steam-bath, an amount equal to less than one molecule of water; but its melting-point was unaltered, and, as it yielded crystals of the free amine on repeated treatment with alcohol, it does not follow that the loss was nothing but water. We could find no satisfactory method of purifying this, or of making a purer substance. The *bromide* obtained in the preparation of the amine crystallizes in scales like those of the bromide of the secondary amine soon to be described, but less soluble in alcohol.

Triparachlorbenzylamine Chlorplatinate, $[(C_6H_4ClCH_2)_3NH]_2PtCl_6$, was made by adding aqueous chlorplatinic acid to an ethereal solution of the base, and washing with water, alcohol and ether; dried at 100°, it gave the following results on analysis:

I. 0.2380 gram substance gave 0.0405 gram platinum.
II. 0.2796 gram substance gave 0.0471 gram platinum.

	Calculated for $[(C_7H_6Cl)_3NH]_2PtCl_6$.	Found.	
		I.	II.
Platinum,	16.54	17.01	16.84

Properties. Pale orange microscopic irregular plates, almost insoluble in water, alcohol and ether.

It is worthy of especial note that Berlin's tertiary chlorbenzylamine melted at 88°–89°, as this is the only case in which we have found the melting-point of the pure substance lower than that of the impure. His chloride melting-point, 170°–175°, crystallized in well-formed rhombohedra with two molecules of water, which it lost *in vacuo*. Our (impure) salt differed from his not only in appearance and melting-point, but also in losing nothing *in vacuo*; and we have never observed any rhombohedra like those described by him, although we have tried very often and under various conditions to obtain them.

Diparachlorbenzylamine, $(C_6H_4ClCH_2)_2NH$. The bromide of this base, separated from the other amines as described above, and purified by repeated boiling with alcohol, was decomposed with aqueous sodic hydrate; the oil thus obtained solidified on stirring, especially if it was touched with a crystal of the substance.

Properties. White radiating bladed crystals; melting-point, 29°; insoluble in water, soluble in alcohol and glacial acetic acid, freely soluble in ether, benzol and carbonic disulphide.

The *chloride* fell as a white precipitate on adding hydrochloric acid to an alcoholic solution of the base; microscopic rhombic and prismatic plates apparently monoclinic, slightly soluble in water, alcohol and glacial acetic acid, insoluble in ether and carbonic disulphide; melting-point 288°.

Diparachlorbenzylamine Chlorplatinate, $[(C_6H_4ClCH_2)_2NH_2]_2PtCl_6$, made by adding aqueous chlorplatinic acid to the alcoholic solution of the base, and purified by washing with water, was dried at 100°, and analyzed.

0.2389 gram substance gave 0,0496 gram platinum.

	Calculated for $[(C_7H_6Cl)_2NH_2]_2PtCl_6$.	Found.
Platinum,	20.90	20.76

Properties. Pale yellow scales (deeper in color than the corresponding salt of the tertiary amine), slightly soluble in boiling water, almost insoluble in cold water and alcohol.

The *bromide* of the base was obtained during the preparation of the amines in white scales very slightly soluble in water or alcohol, insoluble in ether, easily decomposed by aqueous sodic hydrate, and melting with decomposition between 280° and 290°.

The salts just described are identical with those of the α modification of Berlin's secondary chlorbenzylamine; and, as we could find no trace of any other modifications, there can be but little doubt that the β, γ and δ forms of Berlin consisted of mixtures of para- and ortho-compounds, in varying proportions, and this view is still further supported by the fact that the melting-points of these so-called isomeres are very near together, those of the chlorides in fact all lying within ten degrees.

Monoparachlorbenzylamine, $C_6H_4ClCH_2NH_2$, precipitated from the aqueous solution of its bromide with sodic hydrate and distilled with steam forms a colorless oil nearly, if not completely, insoluble in water, but soluble in ether; on exposure to the air it is converted, almost at once, into a white soluble crystalline carbonate; if therefore care is not taken to exclude carbonic anhydride, small quantities of the amine seem to dissolve easily in water.

The *carbonate* was made by exposing the free base to carbonic anhydride or even to the air, and was always left when an ether extract containing the base was allowed to evaporate spontaneously. Crystallized from water, it forms white plates often of considerable size, from alcohol needles; melting-point, 114°–115°; it dissolves slowly in cold, quickly and freely in hot water and alcohol; sodic hydrate sets free the oily amine.

The *chloride* made by dissolving the carbonate in hydrochloric acid crystallizes in long, narrow white plates, soluble in water and alcohol, sparingly soluble in glacial acetic acid, and essentially insoluble in ether, benzol and carbonic disulphide; melting-point, 239°–241°.

Monoparachlorbenzylamine Chlorplatinate, $(C_6H_4ClCH_2NH_3)_2PtCl_6$, made by mixing a solution of the chloride of the base with platinic chloride, purified by washing with a mixture of alcohol and ether, and dried at 100°, gave the following result:

0.3067 gram substance gave 0.0866 gram platinum.

	Calculated for $(C_7H_6ClNH_3)_2PtCl_6$.	Found.
Platinum	28.39	28.23

Properties. Bright yellow branching plates or needles, arranged in round woolly groups when crystallized from water, in which and alcohol it is decidedly soluble.

The *bromide* of the base formed in the preparation of the amines resembles the chloride in appearance and solubility, but is somewhat less soluble in cold water, and melts with decomposition between 225° and 230°.

The foregoing results differ from those obtained by Berlin only in the melting-point of the chloride, which he found 197°; he gives no melting-points for the carbonate and bromide.

To make it easier to compare the new melting-points with those in use heretofore, we have collected them in the following table; the second column of which gives the melting-points of the pure substances made by us, and the third the melting-points determined by the chemists mentioned in the fourth column.

Name of Substance.	True Melting-point.	Old Melting-point.	Authority for Old Melting-point.
Parachlorbenzylchloride . . .	29°	Liquid.	Beilstein and Geitner.
Parachlorbenzylbromide . . .	48½°		
Parachlorbenzylalcohol . . .	70½°	66°	Beilstein and Kuhlberg.
Parachlorbenzylcyanide . . .	29° (?)	Liquid.	Neuhof.
Parachloralphatoluylic Acid . .	103½°-104°	60°	Neuhof.
		68°	Radziszewski.
Parachlorbenzylsulphocyanate .	17°		
Primary Amine	Liquid.	Liquid.	Berlin.
" " Chloride . . .	239°-241°	197°	"
" " Bromide . . .	225°-230°		
" " Carbonate . .	114°-115°		
Secondary Amine	29°	Liquid.	Berlin.
" " Chloride . .	288°	288°-289°	"
" " Bromide . .	280°-290°	283°-290°	"
Tertiary Amine	78½°	88°-89°	"
" " Chloride . . .	196° (?)	170°-175°	"

The revision of the parachlorbenzyl compounds will be continued in this laboratory; in fact, the aldehyde and some of the sulpho-derivatives have been already made and partially studied by Mr. J. Fleming White, whose work will form the subject of a later paper of this series.

ON THE ACTION OF HYDROCHLORIC ACID AND OF CHLORINE ON ACETOBENZOIC ANHYDRIDE.

By Wm. H. Greene.

In a note published in the *Bulletin de la Société Chimique* (32, 164), M. Loir states that acetobenzoic anhydride prepared by the action of benzoyl chloride on sodium acetate is decomposed by hydrochloric acid at 130°, into acetyl chloride and benzoic acid, while at 140° chlorine converts it into acetyl chloride and chlorobenzoic acid; under the same circumstances the anhydride made by the reaction of acetyl chloride with sodium benzoate yields nothing, but at 160° hydrochloric acid converts it into benzoyl chloride and acetic acid—with chlorine at 170° it yields benzoyl chloride and chloracetic acid.

These reactions appeared extremely improbable. Acetobenzoic anhydride begins to decompose at a temperature below 150°, into acetic anhydride and benzoic anhydride; at temperatures near this point it should act with reagents as would a mixture of the two anhydrides. Besides this, M. Loir determined the nature of his decomposition products by putting them in water, and did not, it appears, attempt to fractionate his distillates in any manner. Acetic anhydride is decomposed by hydrochloric acid at ordinary temperatures, and acetobenzoic anhydride, a less stable compound, would hardly withstand the action of the same reagent at temperatures near 100°.

I have repeated the experiments of M. Loir with the following results:

If dry hydrochloric acid be passed into acetobenzoic anhydride at ordinary temperatures, the reaction is the same, by whichever process the anhydride may have been prepared; benzoic acid is deposited, and the tube conveying the hydrochloric acid becomes obstructed. On raising the temperature, acetyl chloride begins to distill at 55-60°, and the product obtained up to 130° is a mixture of acetyl chloride and acetic acid. If the heat be raised much above 130°, and the current of hydrochloric acid rapid, a small quantity of benzoyl chloride is carried over, and will be found in the distillate. The residue in the apparatus consists of benzoyl chloride and benzoic acid. If the anhydride be heated to 130°, or any other temperature, before passing the hydrochloric acid, the reaction is the same with the anhydride prepared by each process. However, it seems that the lower the temperature the greater the proportions of acetyl chloride and benzoic acid which are formed, while at higher temperatures (130–150°) the reaction yields acetyl chloride, acetic acid, benzoyl chloride and benzoic acid in about equivalent proportions.

Chlorine acts in an analogous manner; the products are the same in whichever manner the anhydride may have been prepared; but, with the exception of the acetyl chloride, these products are more difficult to separate than those formed in the reaction with hydrochloric acid. Indeed, chloracetic acid boils at about 186°, and benzoyl chloride at 198°; yet, in the experiments of M. Loir, the latter compound seems to have distilled over first, leaving the chloracetic acid in the retort. At temperatures near 150° the products of this reaction are acetyl chloride, chloracetic acid, benzoyl chloride and o-chlorobenzoic acid; at lower temperatures the principal products are acetyl chloride and chlorobenzoic acid.

From his experiments M. Loir concludes that the constitution of benzoyl acetate differs from that of acetyl benzoate; but the results of these experiments being erroneous, such a conclusion is unsustained. The bodies thus named are identical, all of their reactions *under the same conditions* are the same, and they must be represented by the same rational formula.

ON THE RELATIVE DENSITIES OF PERMANENT GASES AT HIGH TEMPERATURES.

By J. M. Crafts.

The ingenious method* of Professor Victor Meyer for the determination of the density of vapors is too well known to need a description, and many chemists have already recognized by personal observation the great value of this addition to our means of investigation. The unlooked-for observation of an abnormal and peculiar density in the case of chlorine and iodine, which appeared in the month of July 1879, added greatly to the interest already excited by a very remarkable and extended series of observations, and the results of V. and C. Meyer have been commented upon from various sides. Sir Benj. Brodie looks upon them as confirming his theoretical views upon the composition of the halogen group; Prof. Lieben † has given them another interpretation, and some doubts ‡ as to the accuracy of the conclusions have been expressed, but thus far they have not been justified by experiments having a direct bearing on the subject.

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* Ber. deutsch. chem. Gesell. 11, 1867, 2253; 12, 609, 681, 1112, 1195, 1282, 1426, 2204.

† Comptes rendus 89, 253. Professor Lieben's supposition of an abnormal coefficient of expansion has fewer analogies in its favor than Professor Meyer's idea of a chemical dissociation, when it is borne in mind that the phenomenon to be explained is a ⅔ normal density constant within large limits of temperature.

‡ Ber. deutsch. chem. Gesell. 12, 2066. Professor Seelheim recalls certain experiments upon the volatility of the chloride of platinum in a current of chlorine and proposes the equation $Pt_2Cl_4 = 2Cl_2 + Pt_2 = 6$ vols. as an explanation of the ⅔ density attributed to chlorine. His equation is not in accordance with his own figures, since he says that the volume is increased by ⅓, but the equation would suffice to account for the increase of ½ really observed by Professor Meyer. It would appear, however, desirable to support by some more direct experiment the hypothesis that chlorine (even when mixed with a certain quantity of air as it is in Meyer's apparatus) can maintain in a state of vapor 2.77 times its weight of platinum at a temperature of 1200° and that without the intervention of a permanent chemical combination. Professor Dunnington (Chem. News 40, 141) cites some observations upon the difficulty of obtaining platinous chloride in a state of purity.

In the month of September of last year the author expressed to Professor Meyer his desire to repeat the experiments upon the density of chlorine, and was furnished most readily with information regarding the manufacture of the porcelain cylinders and the precautions to be observed in heating them to avoid fracture. The results of these experiments were communicated to the French Academy of Sciences at the sitting of Jan. 26, 1880, and the subsequent paper of Professor Meyer, which bears the date Feb. 25, 1880,* confirms them in regard to gaseous chlorine. As the methods of operating present some differences, and results have been obtained with a number of other gases, the present memoir describes these experiments in detail. They are confined entirely to gases, and chlorine salts of platinum have not been experimented upon, since the employment of gaseous chlorine simplifies the process and leaves less room for varied interpretations of the results.

The principle of the method is the same as that of Professor Meyer's: namely, the displacement of a known quantity of one gas by another, with the necessary precautions to insure that both gases have been heated to the same temperature. The relative densities are in inverse proportion with the two volumes measured before and after the displacement. The accompanying plate gives the general arrangement of the apparatus; but in order to economize space the furnace is not represented, and the capillary tubes which join the two measuring apparatus with the porcelain cylinder are represented somewhat shorter than the reality; these must be adapted to size of the furnace, and must allow the measuring tubes to be sufficiently distant to be protected by a screen from the radiant heat. In these experiments the porcelain cylinder *ab* was heated in a Perrot's gas furnace in exactly the manner indicated in the design published by Professor Meyer,† except that the bottom of the cylinder *a* was not allowed to touch the clay support, but was held in position by a clamp above the furnace, and this arrangement is a most essential precaution in using enamelled porcelain vessels at a high temperature; the enamel must not be allowed to touch a heated surface to which it may adhere. The stem of the cylinder is much less exposed to this danger, because the current of air through the hole in the furnace cover prevents the enamel from attaining the temperature necessary to its fusion.

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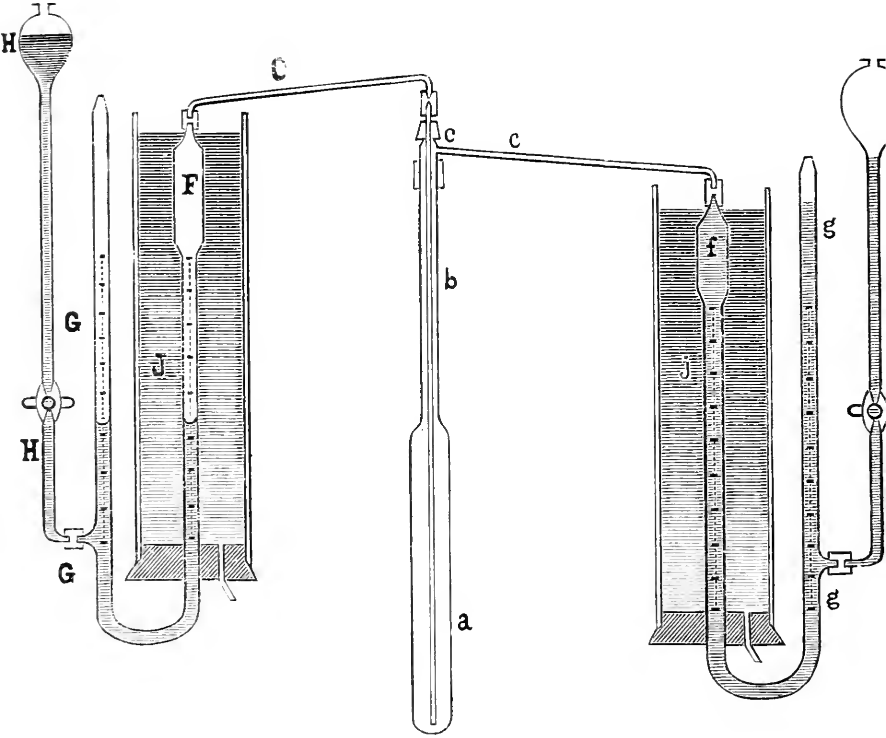
* Ber. deutsch. chem. Gesell. 13, 339.

† Ibid. 12, 1113.



The U tube *FGH* serves to measure a fixed quantity of the gas whose density is to be taken. Since the gas is expanded to about six times its original volume at 1350°, and since it should not fill more than two-thirds of the porcelain cylinder, when introduced into it at that temperature, the measuring tube is made to contain from 10 to 14 c. c., when a porcelain cylinder of 100 c. c. capacity is used. For lower temperatures a larger measuring tube may be used. The error in measuring depending upon the variable quantity of liquid adhering to the sides of the vessel *F*, errors of observation and fault of level in the two branches *F* and *G*, does not exceed 0.02 c. c; consequently it amounts to 0.2 per cent. when 10 c. c. are taken. A number of experiments were made to determine this limit of accuracy, and it may be remarked that the use of sulphuric acid instead of water is not unfavorable to constant results. The measuring apparatus was carefully calibrated with water, and a series of experiments which were made by weighing the quantity of liquid, which the vessel contains under different circumstances (varying the temperature and the time during which the liquid was allowed to flow out) contributed to fix the conditions necessary to obtain constant results. Both branches of the U tube have corresponding divisions to facilitate bringing the liquid to the same level in each. It is only when mercury is used that this operation presents some difficulty. The vessel *H* provided with a cock serves to regulate the pressure, which is kept as nearly as possible equal to the atmospheric during any transfer of gas. *H* communicates with *G* by means of a flexible joint in black caoutchouc, which resists even the action of strong sulphuric acid during several days. The measuring apparatus *fgh* is similar in every respect to the previous one. *F* and *f* are surrounded with water which is changed before each experiment in order to insure that both measuring tubes should be at the same temperature. When the gases are measured over sulphuric acid or mercury it is unnecessary to know the temperature, but sometimes water was used in the tubes *f g*, and then the temperature was measured in order to calculate the tension of aqueous vapor. The tube *FGH* communicates by means of the capillary tube *C* with a platinum tube of about 0.8 mm. interior diameter, which conveys the gas to the bottom of the porcelain cylinder. The piece *cc* allows the displaced gas to flow from the upper part of the cylinder into *f* where it is measured. The joints are made with black caoutchouc of 4 mm. exterior diameter and only 0.7–0.8 mm. interior diameter, and all joints bound with copper wire. The apparatus, when arranged in this manner and attached to a manometer, sustains a vacuum for 24 hours, and frequent trials were made during the experiments to ascertain that all the connections were in good condition.

During all the experiments of the present memoir, as the determination of temperature proved to be little involved in the study of the density of permanent gases, it was thought sufficient to heat the porcelain cylinder directly in the gas flame of the furnace as was done by Professor Meyer, although it is questionable whether an equal distribution of heat is thus obtained. This mode of operating has, however, a serious disadvantage. The enamel of the porcelain is rapidly attacked, particularly on the side where the current of heated gases is most rapid, and the cylinders soon become pervious to hydrogen and to aqueous vapors, but not to other gases. A large number of determinations were made of the quantity of water which passed through the porcelain during a given time, when it was exposed at a high temperature to the products of combustion, and the quantity was found equal to 0.001–0.002 gram per hour, and accordingly the quantity which penetrates during the five to ten minutes that an experiment lasts is too small to affect the results, but it is essential to fill the porcelain cylinder directly before each experiment with dry gas. There is probably little unburnt hydrogen in contact with the exterior surface of the porcelain, and the diffusion of this gas only becomes noticeable in experiments in which the cylinder is filled with it.

It is only necessary that the temperature should remain constant about five minutes, and that no perceptible loss or gain of gas should occur during that time, to make a determination of density possible under favorable conditions, and usually no experiment was made until the volume of gas in the closed apparatus had remained constant during ten minutes. In order to determine how quickly the interchange of temperature takes place between the cold gas introduced into the apparatus and the heated gas which is displaced, a series of experiments were made with air displacing air, by forcing into the porcelain cylinder 10 c. c. of air, and by detaching the vase *fgh* after a given interval of time to measure the volume of air displaced. It was found that within the limits of error already mentioned the 10 c. c. taken in the apparatus *FGH* were found again in *fgh* after about one minute, and that there was no further change of volume; hence a result obtained after the first minute may be taken as exact, and the very short time required for an experiment enables determinations to be made under unfavorable circumstances, when observations of longer duration would be complicated by phenomena of diffusion and other causes of error. It follows then that the comparison of the density of two gases at any temperature which can be supported by a porcelain apparatus is a very simple and rapidly executed operation.

The details of the process are these: The heated porcelain cylinder is filled with the gas which is to serve as the standard of comparison, by conducting it first in a rapid, and finally in a slow current through the platinum tube until all traces of other gases are expelled. It is usually preferable to choose the lighter of the two gases for this operation, which lasts from five to ten minutes; as soon as it is concluded the rubber connection at the end of the platinum tube is closed, the measuring apparatus *fgh* is attached to the capillary tube *c*, and observations of the level of the liquid in *f* are made until a constant position, during five minutes at least, indicates a constant temperature.* When the temperature of the furnace is constant that of the porcelain cylinder becomes stationary in two or three minutes, because the slow current of gas which is passed through at the last abstracts very little heat. The level of the liquid in *f* is set at zero, the platinum tube is left open for a few seconds in order that the gas may take the atmospheric pressure, and it is then connected with the capillary tube *C*, and a known volume of gas, measured in *F* also under the atmospheric pressure, is forced into the porcelain cylinder, and the corresponding volume of gas displaced is measured in *f*, taking care to regulate the outflow of the liquid so that the level is the same in the two branches. It is easy to test and correct an error from this source by noticing the change of level, if any, that takes place on allowing *f* to communicate again with the air. The diffusion of the two gases destroys the value of the comparison between their densities after a few minutes, but if their coefficients of expansion are the same, which appears to be nearly the case in all the permanent gases that have been thus far examined, no difference in the results is apparent. In the case of chlorine several analyses were made of the gas which had passed over into the measuring tube *f*, and it was found after about five minutes to contain two or three per cent. of chlorine, so that if the density had proved decidedly abnormal, as seemed at first possible from Professor Meyer's researches, it would have been necessary to have taken this quantity into consideration.

It is scarcely necessary to add that the gases operated upon must be perfectly dry, and consequently water can only be employed in the measuring tube *fgh*, and it is usually more convenient to fill both tubes with sulphuric acid or with mercury.

The following experiments were made with chlorine prepared in the usual way with peroxide of manganese, that had been left several days in contact with hydrochloric acid to decompose carbonates. The flask was not heated higher than 25° during the evolution of the chlorine. It is easy to measure this gas over sulphuric acid, and the

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* The changes of temperature of the gases in these operations are extremely rapid and are probably nearly completed in the capillary tubes, so that the gas which reaches the bottom of the porcelain apparatus and that which passes out through the tube *c* have nearly acquired the temperature which they should have at the moment of measuring them. The low specific heat of gases enables them to assume the temperature of the surface layer of the material enclosing them, and this property is very favorable to the performance of these determinations of density. 23 grams of glass in cooling one degree heat 10 c. c. of a gas to 1300°.

only precaution necessary is to expose the acid in the measuring tubes during one or two hours to an atmosphere of chlorine in order that the slight absorption, which takes place, may be complete. As the liquid is not afterwards agitated in presence of the gas, no appreciable absorption or disengagement takes place. Chlorine attacks black rubber very slowly, and diminution of volume is observable from this source after a few minutes; but, rejecting the first experiment in which fresh surfaces are exposed, the subsequent ones gave approximately accurate results. The platinum tube is not readily attacked in the parts which are cold nor in those which are strongly heated; but a zone of one to two centimeters in length, which has a temperature of 400 to 500°, is more rapidly attacked; and although the tube is not actually eaten away, the passage of a current for several hours makes it brittle and crystalline. It lost about 0.01 gram in weight in half an hour in each of two experiments, the total weight of the tube being about 40 grams.

10	c.c. of chlorine displaced	9.41	c.c. air	1st	experiment.
10	" " "	10.43	" "	2d	"
10	" " "	10.30	" "	3d	"

If the apparatus is filled with chlorine and 10 c.c. of air are introduced the results are less satisfactory, on account of the formation and decomposition of chloride of platinum on the outer surface of the tube, when it is not heated red hot and is exposed to a mixture of chlorine and air of variable composition.

The platinum tube was replaced in the following experiments by a clay pipe stem, deprived of the glazing which hardens the exterior surface, and which often appears to contain lead.

10	c.c. of chlorine displaced	10.37	c.c. air	1st	experiment.
10	" " "	10.24	" "	2d	"

In order to meet the objection that part of the chlorine had been absorbed by the pipe stem, giving an apparent density higher than the real, the experiment was reversed, and air was passed into the porcelain apparatus filled with chlorine.

10	c. c. of air displaced	9.98	c. c. chlorine.
10	" "	10.00	" "

It will be noticed that these results vary two or three per cent., and leave the question unsettled whether the density of chlorine compared with that of air is exactly normal or slightly less than the normal density, but they were chiefly undertaken to ascertain whether under these circumstances chlorine would be found to expand one and one-half times as much as air at a high temperature, as Professor Meyer had concluded from his experiments with platinum salts, or whether the density is nearly normal, and these observations amply suffice to resolve this problem. In view of the two-third density which had been found for chlorine it was thought necessary to examine the possibility of the absorption of chlorine by the clay pipe stem, and the subsequent abandonment of the chlorine in the presence of air. Had this phenomenon taken place in two series of experiments above, the absorption of exactly 5 c. c. in the first case and the evolution of 3.33 c. c. in the second case would disguise an abnormal density and give the apparent density stated above. This extremely improbable hypothesis was tested by placing beforehand in the cylinder enough fragments of pipe stem to double the volume of this material, and consequently double its effect. An experiment made under these conditions gave the same results as before, 10 c. c. of chlorine displaced 10.20 c. c. of air.

The hypothesis that chlorine may be a compound of oxygen has been revived and associated with the results of Professor Meyer. The following equation for example, which would explain the two-third density, has been proposed as a guide to further investigations,* $2\,(M_2O_2) = 2\,(M_2O) + O_2$. M represents the hypothetical element, murium. It appeared that hydrochloric acid might give an abnormal density of unforeseen value, according as the hydrogen, favoring this dissociation, combined chiefly with the murium or with the oxygen. A series of experiments was made with pure and perfectly dry hydrochloric acid measured over mercury.

10 c. c. of this gas displaced 10.03 c. c.; 9.93 c. c.; 9.97 c. c. of nitrogen; and 10 c. c. of nitrogen displaced 9.73 c. c.; 9.61 c. c.; 9.68 c. c.; 9.63 c. c.; 9.73 c. c. of hydrochloric acid.

The loss, particularly in the second series where the apparatus was filled with hydrochloric acid, may depend upon an absorption

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* Mention is made in a lecture given by Professor Meyer, and reported by Mr. Watson Smith in the *Chemical News* 39, 49, of the production of oxygen by passing chlorine through a heated porcelain cylinder and absorbing the undecomposed chlorine by iodide of potassium. The penetration of aqueous vapor into the heated cylinder may perhaps account for the formation of small quantities of oxygen, according to the equation of a partial reaction $H_2O + Cl_2 = 2\,HCl + O$, as it has been shown that the chlorine would be in presence of water under these circumstances

with the rubber connections or by the heated porcelain. It increases with the duration of the experiment and amounts to 1 or 2 c. c. in an hour; but these experiments suffice to demonstrate that the density of hydrochloric acid is nearly normal. It is essential to use nitrogen and not air in these experiments at a high temperature, since oxygen causes a partial combustion of the hydrochloric acid, and the loss is increased by 0.2 to 0.3 c. c.

Hydrochloric acid does not act upon porcelain at a high temperature with formation of any gaseous product and serves admirably to expel other gases from the cylinder, its ready absorption by water offering a means of separating it from them. Two experiments in which hydrochloric acid was passed for half an hour through a porcelain apparatus at a bright red heat gave only 0.2 to 0.3 c. c. of gas unabsorbed by water. These facts were taken advantage of from the beginning of these investigations to devise a new and convenient process for the estimation of high temperatures, which will be described later. All the experiments in this paper were made at the highest temperature obtainable with a small Perrot's furnace, and various measures fix it between 1300° and 1400°, but the exact measure of the temperature and the mode of heating acquire far greater importance when the density of a gas varies with the temperature as is the case with iodine, and special attention is devoted to this subject under that head.

The determination of the density may serve as a measure of the dissociation of those gases which combine with diminution of volume, and consequently are decomposed with augmentation of volume, like steam, carbonic acid, ammonia, &c., and experiments were made with carbonic acid to ascertain whether dissociation could be detected by this means at 1300°–1400°.

10 c. c. of carbonic acid displaced 10.03 c. c., 10.01 c. c., 10.00 c. c., 10.03 c. c., 9.95 c. c. and 10.09 c. c. of nitrogen.

10 c. c. of nitrogen displaced 9.95 c. c., 9.91 c. c., 9.98 c. c. and 9.93 c. c. of carbonic acid.

In this case in which the gases operated upon do not attack the rubber connections, and are not affected by moisture, the results correspond very closely with each other, and show that if dissociation takes place under these circumstances it is to a very slight extent.

The difference of density noticed may be attributed to a different coefficient of expansion, and the first series of experiments shows that the 10 c. c. of carbonic acid occupy at 1350° 1.002 times the volume that 10 c. c. fill at the same temperature. The second series of experiments gives the number 1.005 as the value of the same relation. If the coefficient of expansion of nitrogen is 0.00367, that of carbonic acid is 0.003677–0.003688 between 0° and 1350°. The coefficient of expansion of carbonic acid between 0° and 100° at a constant pressure has been determined at 0.00371 by Regnault,* and a diminution of this value as the temperature is farther removed from the boiling point of carbonic acid, until a constant coefficient equal to 0.00367 is reached, would give the mean coefficient observed in the above experiments.

A long interval of temperature diminishes proportionally the importance of numerical errors, and if the means of investigation were equally exact the coefficient established above would have a probable error 13.5 times smaller than that obtained between 0° and 100°; and although it is probable that various causes diminish the value of results obtained at high temperatures, it is to be noticed that the single experiments, and even the two series compared with each other, are as concordant as the experiments of Regnault; but these observations are not regarded as conclusive upon the coefficient of dilatation of carbonic oxide, and experiments will be undertaken by a different process to control this important factor.

A number of experiments were made with hydrogen which have not given precise results because the porcelain cylinder, heated directly in the flame of the furnace, allows hydrogen to penetrate the enamel. They seem to point to a lower coefficient of expansion for hydrogen than for nitrogen; further experiments will be made upon this subject with different modes of heating.

The only other permanent gases with which it is possible to make experiments with this apparatus are the oxides of carbon and compounds of nitrogen. The oxides did not seem likely to offer any new features of interest, but some observations were made upon the decomposition of ammonia which will be described in the next paper.

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* Mémoires de l'Académie, 21.

THE VAPOR DENSITY OF IODINE.

By Fr. Meier and J. M. Crafts.

The memoir of V. and C. Meyer,* referred to in the preceding paper, contains the statement that the vapor density of iodine presents the same curious anomaly which they found for chlorine, namely a constant density equal to two-thirds the normal at all temperatures above 1000°–1200°, and consequently they look upon this phenomenon as confirming their original views regarding the constitution of chlorine. At that time no distinction had been made between chlorine employed as a gas or disengaged from a platinum salt; and since one of us had failed to discover a peculiar density for chlorine, it was thought advisable to examine carefully that of iodine, as the case seemed simpler than that of the decomposition of a platinum salt.

This work was ready for publication before the appearance of the last paper of Professor Meyer,† in which he finds two distinct densities for chlorine, and gives a series of determinations of the density of iodine at different temperatures. The work with gaseous chlorine by a modified process is nearly in accordance with the results described by one of us, but our results with iodine differ notably from those of Professor Meyer, and we do not regard them as confirming his theoretical views. We venture therefore, after consulting with him, to place our results beside his with the details necessary to a comparison of our different methods of operating, which may perhaps suffice to explain the differences in our conclusions.

When the investigation was first undertaken it seemed to us especially important to seek for the cause of the different value, which is obtained for the vapor density of iodine by the method employed by MM. Sainte Claire Deville and Troost in their classic research‡ which extended so greatly the range of experiments in this direction. They found the vapor density of iodine normal at 860°–1040°, and used it as a standard of comparison for the determination of other densities. Since the publication of the results of V. and C. Meyer, and also of a brief abstract§ of those

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* Ber. d. d. chem. Gesell. 12, 1431.

† Ber. d. d. chem. Gesell. 13, 399.

‡ Annales de Chim. et de Phys. 58, 257.

§ Comptes rendus.

contained in the present paper, which we communicated to the French Academy of Sciences, M. Deville* has modified his apparatus for obtaining a constant temperature, and proposes to repeat the experiments with iodine. It is best therefore to withhold all speculations upon this question until this work is completed.

The manner in which Professor Meyer has grounded upon his experimental data some most ingenious hypotheses appears to us to add greatly to the interest of the question, and believing that we do not misconceive his intentions in regarding these views rather as guides to further research than as definitely established theories, we desire to discuss them with reference to their probable value in supporting and co-ordinating his facts. We have not repeated the experiments with chloride of platinum, which led Professor Meyer to the molecular weight 47.3 for chlorine at high temperatures, but our views regarding the question are influenced by our failure to obtain similar results with iodine, which according to Professor Meyer presents the same phenomenon of a density equal to two-thirds the normal.

The nascent state of chlorine set free from platinous chloride and the hasty ("brusque") volatilization of bodies are offered† as an explanation of the difference of density between chlorine from platinous chloride and chlorine employed in the gaseous state, and the rapid heating of solid iodine is supposed to be a partial explanation of the difference of density obtained by Meyer's or Deville's process. It appears to us doubtful whether the term nascent state can be applied to a condition which subsists during several minutes at 1500°. The conception, which at the best is somewhat vague, of the nascent state has been evoked to explain some chemical phenomena in which it is usually possible to attribute an important part to the influence of the mother substance—influence which extends throughout the duration of the reaction. Here, however, the chlorine must be considered as removed from all influence of the platinum as soon as it acquires the gaseous state. It is possible to conceive a distinction between chlorine born of a union with a noble metal like platinum, and ordinary chlorine; and this point of view has analogies with that of Schönbein for ozone and autozone, but only, as it appears to us, when the phase through which the density of chlorine passes at about 700° is disregarded. Oxygen is disengaged from certain com-

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* Comptes rendus, 90, 773.

† Ber. deutsch. chem. Gesell. 13, 401.

pounds as ozone, and retains its peculiar molecular weight so long as it remains ozone; but according to Professor Meyer chlorine from all sources has a normal density at about 700°, and the abnormal density only appears at higher temperatures. Chlorine must pass through the temperature of 700° to arrive at a higher, and it does not appear why the molecules which have reached a normal density (molecular weight) at 700° should be dissociated in one case more than another, supposing that this stage may be taken as a new point of departure. If it is insisted, upon the other hand, that differences in the constitution of chlorine are produced by a more or less rapid decomposition of its platinum salt, it may be objected that by varying the size and the material of the vessel containing it, which is thrown into the porcelain cylinder, the disengagement of the chlorine may probably be rendered as slow at 1200° as at 700°, and a further experimental development of the hypothesis seems desirable from this point of view. It would be interesting, for example, to ascertain if liquid chlorine, very rapidly heated, would have an abnormal density. An affirmative result would give an important confirmation to Professor Meyer's views, but it must be added that a negative one would not suffice to invalidate them.

Some thirty experiments made with iodine have not revealed anything which would induce us to suppose that iodine changes its density according to the rapidity of its volatilization, but the condensation of the substance in the stem of the porcelain cylinder opposes an obstacle to experiments of long duration, and this reason obliged us to abandon the study with this body of the interesting question of the function of time* in a very simple phenomenon of dissociation.

The iodine used in the following experiments was purified by the method described by M. Stas, except that instead of being simply

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*The study of such questions is much easier in the case of permanent gases, and although thus far we have not been able to observe with them a phenomenon of dissociation, one of us has made a few experiments upon the rate of decomposition of ammonia by introducing this gas into a porcelain cylinder heated bright red hot. In the first experiment the cylinder was filled with pure nitrogen and 10 c. c. of ammonia were introduced; after one minute the volume of nitrogen displaced was 10.4 c. c.; after three minutes, counted from the commencement, the volume was 10.53 c. c.; after five minutes it was 10.60 c. c. and after seven minutes it was 11 c. c.

In a second series the cylinder was completely filled with ammonia, and the volume read. After one minute an increase of volume equal to 5 per cent. of the whole was observed.

These experiments were not carried further with the apparatus described in this memoir, because it appeared preferable to make them with an air thermometer with capillary stem, so mounted as to enable the pressure or the volume to be measured at will.

digested with iodide of potassium, it was heated several hours at 150° in a sealed tube with a concentrated solution. The addition of water gave several fractional precipitations from the solution in iodide of potassium, which were collected separately; the first four gave identical results, and only the first three were used in the subsequent determinations of density. Each portion was distilled with steam, dried over nitrate of calcium* rectified several times over anhydrous baryta and sublimed. The iodine thus obtained solidifies at 112.7°–113° (with correction) when the thermometer is immersed in the liquid. The correction for the part of the stem of the thermometer which is not heated is easily made by plunging it to the same point in the vapors of boiling water.

Determinations of the density of this iodine made with a glass apparatus in boiling sulphur give results corresponding exactly with the calculated density 8.786 if certain precautions are taken, the necessity of which will be best appreciated on considering the results obtained under different conditions.

The form of apparatus which we consider preferable is one similar to an air thermometer with constant pressure, and the process consists in introducing the weighed substance into the apparatus, which is hermetically closed before the operation begins, and then measuring the increase of volume corresponding with the volatilization of the substance.

We give only the drawing of the apparatus intended for use at high temperatures, which will suffice to explain the general arrangement adopted in all cases. For experiments in boiling sulphur an iron tube, closed at its lower extremity, is substituted for the parts *m*, *n*, and *o*. This tube is 60 cm. long, 5 cm. wide, and has an iron collar about 35 cm. from its lower end, which supports it in the heating apparatus. This latter consists of two concentric cylinders to prevent loss from radiation, with a chimney on the side, and a Bunsen's lamp is so arranged at the bottom that the flame is not deflected by drafts. A series of holes in the upper part of the inner cylinder allows the equal exit of the air on all sides. It is easy to keep the sulphur boiling, so that the condensation is complete at about 10 cm. below the top of the iron tube, which is closed with a cork through which the stem of the glass cylinder passes. The cylinder *a* is plunged in the liquid sulphur, and when the ap-

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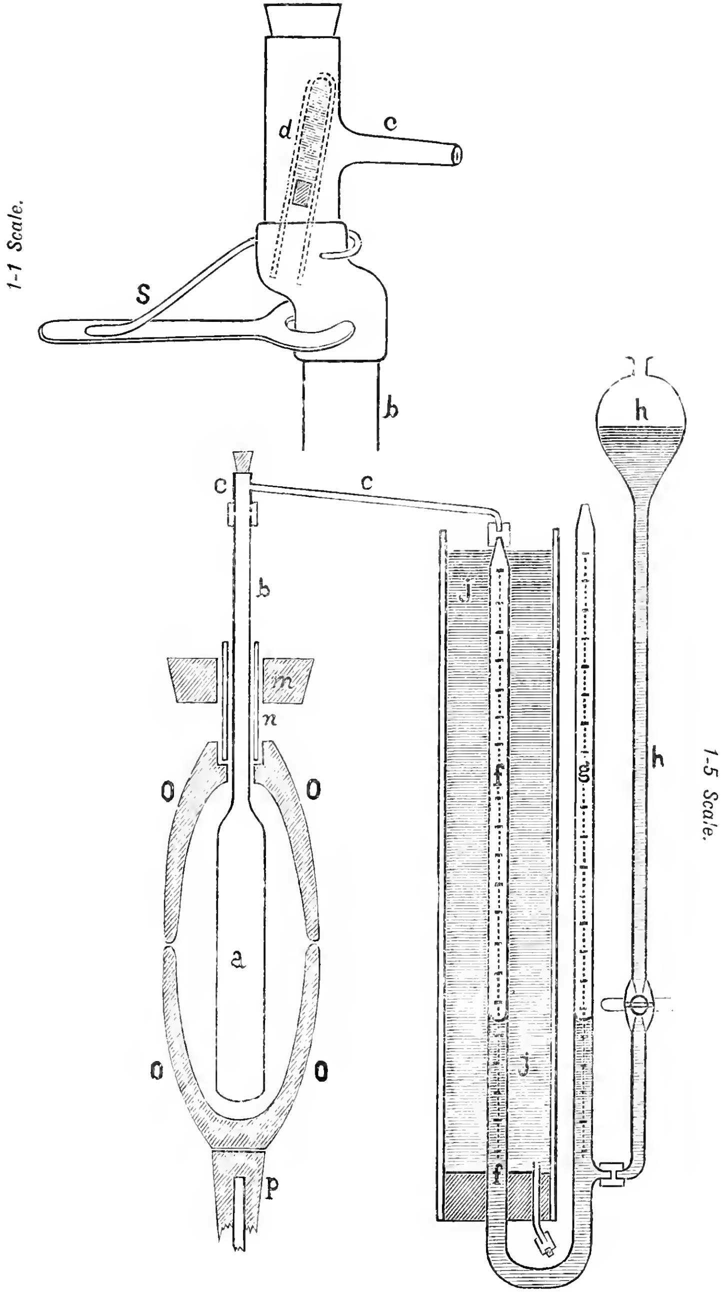
*M. Stas says that all other modes of drying introduce impurities. We doubt if they would have affected our results, but the method was adopted to exclude all possible sources of error.

paratus is well arranged it is easy to maintain a temperature so constant that the change of volume in the measuring tube *f* does not exceed 0.01 c. c. during ten minutes. The form of the cylinder *ab* has considerable influence upon the results, and we have made a series of experiments to determine what are the most favorable dimensions. It appears from these experiments that the shape of the lower part *a* is of little consequence, provided it can be heated equally in all parts, since the vapors even in a cylinder of large diameter act during the first few moments like a piston and drive the air out before them, then the diffusion becomes more noticeable, and must be retarded as much as possible by a long narrow stem. The cylinders which we eventually found the most convenient had a capacity of about 150 c. c. The part *a* was about 4 cm. wide and 13 cm. long, and the part *b* was 40 cm. long and 3 to 4 mm. wide (interior diameter).

The following experiment demonstrates to what point the observations can be prolonged before they are vitiated by the diffusion and subsequent condensation of iodine. 0.1266 gram of iodine was volatilised in such an apparatus, and the volume of air displaced measured in the tube *f* was equal to 12.48 c. c. after two minutes; after three minutes (counting from the beginning) 12.52 c. c.; after four minutes 12.51 c. c.; after five minutes 12.49 c. c.; after eight minutes 12.47 c. c.; after 25 minutes 11.59 c. c. The beginning of the diminution of volume usually coincides with the appearance of a slight cloud of iodine vapor in the stem above the mouth of the iron tube.

It is evident that the apparatus *fgh* can be closed at any moment and removed to read the volume at leisure, but it is unnecessary to allow a considerable time to elapse before making the reading, as it was determined by direct experiments that the gas in *f* did not require more than a minute to take the temperature and the tension of aqueous vapor from the surrounding water. The use of a long narrow tube, whose sides are constantly moist, favors the rapidity and accuracy of these observations. It may be here noticed that the formula employed by Professor Meyer to calculate his results presupposes the air in the cylinder *ab* to be perfectly dry, and it is necessary to provide that it is actually so by the careful introduction of dry air before each experiment, otherwise a considerable error may ensue according as the atmosphere is more or less moist. It is important to melt the substance in the


1-1 Scale.
d
c
S
b
c
c
b
m
n
o
o
a
o
o
p
h
j
f
g
h
j
f
1-5 Scale.

little cylinder *d* before weighing it, and to direct the opening downwards in order that the jet of vapor which issues from it may not be turned toward the stem *b*. The accompanying sketch represents the apparatus as arranged for an experiment at the highest temperature in a Perrot's furnace, and in the description we will give in detail the reasons which induced us to modify the original form proposed by Professor Meyer.

The capillary tube *c* communicates freely with the measuring tube *f*, while in the original apparatus the gas was obliged to pass through a layer of water to enter the measuring tube, and the friction and capillary resistance of the water in the tube *c* occasioned loss. In order to estimate the importance of this source of error we arranged an apparatus precisely as described in the *Berichte*, 11, 2254, and forced into the cylinder *ab* 10 c. c. of air without heating. Only 9.5 to 9.65 c. c. of air were forced out of the cylinder into the measuring tube, and it was found that it required an excess of pressure of 6 to 10 cm. of water to make the gas flow out through the capillary tube *c*, although this was only plunged 1 cm. below the surface of the water. This loss of gas does not necessarily occasion an error in the ultimate result, when operating in the manner described by Professor Meyer, as we shall explain later; but his apparatus does not indicate readily a change of tension of the heated gas, and consequently is not very sensitive to changes of temperature.

It is easy to find the correction for the quantity of air displaced by the cork *e*, particularly when it is so small that the volume in question does not exceed 0.2 c. c.; but we have observed an error, which arises when the apparatus is closed at the moment that the vase *d* with the substance is allowed to fall into it, and which appears not to have been noticed by those who have thus far used the process, and a long series of observations which we had made at high temperatures are rendered of little value by this error. We were led to its discovery by certain indications which made us suspect the accuracy of our results, and its nature is sufficiently evident from the following experiment. If the little cylinder *d* without any volatile substance is allowed to fall into the heated cylinder *ab*, and the stopper put in its place as quickly as possible, an increase of volume of 0.4 to 1.0 c. c. is obtained, according to the temperature and the size and material of the vase. If the stopper is put in its place before the vessel *d* is allowed to fall into *ab*, a sudden elevation of the liquid in *f* may be observed while *d* is falling, consequently there is an inward current of air at that instant, which is quickly succeeded by the inverse movement, which proceeds more slowly until the liquid has fallen to its original level after a minute or a minute and a half. Thus in the ordinary manner of making a density determination air enters while the substance is falling and before the cork is put in. The air is probably in part forced in by the passage of the falling body through the tube *b*, but the sudden cooling of the air in *a* seems to contribute still more decidedly to this effect, at least the quantity of air that enters seems to depend more upon the temperature and the weight of the cylinder *d* than upon its size. The error from this source is so nearly a constant quantity that it is possible to determine its value for fixed temperatures and constant conditions by making experiments with a vessel containing no substance, and the results can be applied as a correction to series of determinations of density made under the same conditions, and we give further on a number of results corrected in this way.

The two errors mentioned are in inverse direction and tend to compensate each other in Professor Meyer's experiments at a high temperature, while at lower temperatures they have little influence on the results, whenever it is possible to discriminate between the two phases of the process and reject the first few bubbles which are disengaged immediately after closing the apparatus, but in the present case it has been thought preferable to remove all causes of uncertainty by modifying the apparatus. We suppose that these differences in the mode of operating, and probably others that we have not recognized, may explain the differences in our results. We believe that Professor Meyer has made some experiments with a closed apparatus, and he communicated to us several methods of allowing the cylinder *d* to fall after the cork has been put in its place, and according to our views such determinations should give too low results because the gas was still obliged to pass through a layer of water. This communication was made after all our experiments were made, and as our form of apparatus differs from that proposed we will describe it in detail.

The part *cc* which is connected with the stem *b* by means of a caoutchouc tube is pushed aside by a sort of key *s*, so that *d* is supported by *b*; the apparatus is thus closed, the position of the water in *f* is read, and the substance tube *d* is allowed to fall into the heated cylinder by a movement of the key *s*, which is immediately returned to its first position, and the second reading taken which corresponds to the air displaced by the vapors. This arrangement appears to us the one which best accomplishes its object without change of volume or leakage. For high temperatures the iodine was weighed in a little closed cylinder of platinum, and a loosely fitting stopper of platinum prevented the substance from falling out when the cylinder was inverted. It is well to make the cylinder *d* rather heavy (2.5 to 3 grams) in order that it may not become sufficiently heated to volatilize the iodine before reaching the bottom.

The measuring apparatus *fgh* is precisely similar to the one described in the last paper, except that the graduated tube is not enlarged at the top.

The other changes which we have made in the process of Prof. Meyer concern the method of heating, and are destined to insure an equal distribution of heat. If a platinum wire be introduced through the whole length of a Perrot's furnace, the light emitted in different parts shows by its intensity that the wire is not equally heated throughout its length, and it appears to us doubtful if a porcelain cylinder can be equally heated from top to bottom in the naked flame whose temperature varies like a Bunsen's flame in different horizontal zones; we therefore chose a furnace nearly twice as large as that employed by Professor Meyer,* and the porcelain cylinder was surrounded by a muffle. That employed at the highest temperatures is represented by the parts *oo* in the drawing. It can be easily made from two French crucibles, the upper one of which is pierced with a hole through which the stem of the cylinder *b* passes. The tube *n* which passes through the cover *m* and fits into the upper crucible protects the stem *b* from the direct action of the flame. The furnace is not represented in the drawing, because, except the difference of size, it is precisely similar to that shown in the plate *Berichte* 12, 1113, and the capillary tube *c* is represented much shorter than the reality, and as with the previously described apparatus the measuring tube must be sufficiently distant from the furnace to be protected by a screen from the radiated heat.

For temperatures ranging from 500 to 900° we employ a lead bath weighing about 11 kilograms, which is heated in a Perrot's

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* The inner dimensions of the fire space are in ours, height 275 mm. and width 145 mm.

furnace. The porcelain cylinder is placed inside one of thin iron to protect it from immediate contact with the lead. So large a mass of metal was taken in order to insure an equal distribution of heat. In the course of time the iron tube is oxydized and eaten through at a line sharply marked by the upper surface of the molten lead.

We have made a number of experiments to attempt to establish the degree of temperature which corresponds with a certain quantity of gas burned in a Perrot's furnace, but without being able to do so in a satisfactory manner. Professor Meyer adopted this expedient, using a graduated gas-cock to regulate the supply of gas and taking care to heat always under similar conditions. We measured the gas with a meter which gave the numbers of litres per minute, but the temperatures do not correspond with the quantity of gas alone, but also with that of the air which is passed through the furnace at the same time; thus the temperature frequently falls as the heating is continued because an increased draft from a hotter chimney draws too much air through the furnace, and on the other hand on pushing the furnace to its maximum temperature it is easy to increase the flow of gas beyond the point of perfect combustion and thus obtain a lower temperature, the gas being burnt in part in the lower part of the chimney. We have not been able to devise any means to measure even approximately the quantity of air which is used in a given time, or even to regulate it so as to obtain at will in different experiments identical temperatures. The variations may amount to 100° between 1000° and 1200°. The highest heat obtainable under definite conditions can be fixed more closely. On the other hand we are in perfect agreement with Professor Meyer in saying that the temperature can be maintained sufficiently constant during an experiment, or even during several.

In choosing a method for measuring the temperature we have thought it best not to employ the one founded on the heat imparted to a platinum cylinder, because the differences of form and material in the case of platinum and the additional difference introduced by heating it in an iron cylinder appears to us to leave room for uncertainty whether the temperature measured is really the same as that attained by a porcelain cylinder heated in the naked flame. We have already said that the flame of a Perrot's furnace is not at the same temperature throughout its whole length, and we have endeavored to remedy as far as possible this defect by using a very large furnace and surrounding the porcelain cylinder with a muffle, and this mode of heating appears to us to give better guaranty for the correct determination of the temperature than one in which a porcelain cylinder 20 cm. long and of about 100 c. c. capacity is allowed to pass from top to bottom of a furnace, and consequently through several zones, while the combustion is very different, and then instead of measuring the temperature by heating on another occasion a platinum cylinder of only 4.5 c. c. capacity in an iron tube* in the same furnace, the operation is performed in the porcelain cylinder.

Our attention was attracted to the details of Professor Meyer's calorimetric experiments by the very high temperatures which he obtained,† and we would remark in this connection that the co-

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* The only experiment which we have made to ascertain whether two cylinders, one of iron, the other of porcelain, acquired equal temperatures in the same furnace, gave no indication of a difference. Palladium does not melt in one or the other, although it melts readily in the flame; consequently, this experiment, so far as it goes, offers no positive evidence against the use of an iron cylinder. M. Violle, however, in recent calorimetric experiments, has thought it advisable to heat a block of platinum in a porcelain cylinder placed beside a porcelain air thermometer in a muffle.

† We give some of the latest determinations of high temperatures to serve as points of comparison:

1877 Violle, Comptes rendus 85, 543.
1878 " " " 87, 981.
1879 " " " 89, 702.

Platinum	melts at	1779°.
Palladium	"	1500°.
Iridium	"	1950°.
Copper	"	1054°.
Gold	"	1035°.
Silver	"	954°.

These results agree well with those of M. Ed. Bequerel, Annales de Chim. et de Phys. 68, 73, who gives the melting point of silver at 960°, and that of gold at 1092°. He supposes platinum to melt at about 1580°.

Bequerel, Annales 68,114, found the following temperatures to correspond with the color of the light emitted:

500° - 550° = very dark red
550°—960° = orange red.
960° = yellowish.
1100° = yellowish white.

M. Deville, Comptes rendus, 56, 195, gives the melting point of platinum at 1900°, and considers white heat obtained by burning gas retort carbon with an artificial draught to be 1100°-1300°.

Deville, Annales, 58, 301, says that 1162° is almost white heat, at which the most infusible cast iron becomes liquid.

Valerias, Acad. Belge. Bull. 2, 38, 1874, gives the following as the theoretical limits of the heat of combustion:

Hydrogen burnt in air = 1254°.
Oxide of carbon " " = 1430°.
Ethylene " " = 1612°.

It is evident that the theoretical temperature cannot be nearly attained in a process of combustion, but on the other hand it is to be remarked that these temperatures are estimated from zero as the initial temperature, and that the heat obtained with previously heated gases is efficient of specific heat of platinum which he employs is lower than that which was obtained by M. Violle in the latest work on this subject. For example, it appears from the data in the *Berichte*, 12, 1428, experiments F 1 and 2, that the coefficient used in calculating the highest temperatures was 0.03938, but if the formula $(C_0^t = 0.0317 + 0.000006t)$, which was established by M. Violle to represent the mean specific heat of platinum between 0 and 1100°, is extended to 1500°, the value 0.0403 is obtained, and if it is used in the calculations of Professor Meyer a lower temperature by about 50° is obtained. This result is probably still too high, as the specific heat of platinum probably increases still more rapidly as its point of fusion is neared; and the same may be said of the number given by M. Violle for the melting point of palladium (1500°), which is to be regarded as too high for a similar reason. We used this point as a test of temperature and convinced ourselves by a number of experiments that palladium* could not be melted in a porcelain cylinder heated in the manner described by Professor Meyer in a Perrot's furnace, although this metal melts readily in the flame; we conclude that the temperature does not reach 1500°, and in our first series of experiments with the smaller furnace we have not reached 1400° in our measurements with an air thermometer.

We will describe in detail the process which has been employed by us during the last three months for measuring temperatures, and of which a brief notice has been published;† it is identical in principle with that which Professor Meyer has used in his latest investigation to compare the density of two gases, and indeed if the capacity of the apparatus employed by him were determined,

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greater, but it can not be calculated with our present knowledge of the laws of dissociation and of the specific heat of gases combining with condensation.

Rosetti, Deut. chem. Ges. 10, 2054, gives determinations of temperature in different parts of a Bunsen's flame 17 cm. long which agree tolerably well with the calculated numbers.

Colorless flame mantel	1350°
Violet zone	1250°
Inner blue flame	1200°

These measurements were made with an electric pyrometer graduated by comparison with specific heat determinations, but it is obvious that the high temperature obtained by burning heated air and gas in the outer flame mantel depends upon the form of the flame, and a temperature high enough to melt platinum may be obtained with a good blow-pipe flame. The lower part of the flame corresponds to the heated iron tube in a hot air blast furnace. M. Debray says that platinum can even be melted in the flame of a candle.

* We are indebted to the kindness of M. Debray for a piece of perfectly pure palladium.

† Comptes rendus, March 15, 1880. In this communication we omitted to state that nitrogen and not air was used at high temperatures.

the temperature could be calculated from his published results. The method consists in filling the porcelain cylinder *ab* with dry nitrogen, and as soon as the gas has taken the temperature of the apparatus, it is expelled by another gas and collected in a measuring tube. It is essential to choose for this purpose a gas which can be easily separated from nitrogen, and we have used successfully carbonic acid and hydrochloric acid, and give the preference to the latter, because its instantaneous absorption by water marks well the moment when the operation is finished. It required about two minutes to expel the nitrogen, and the current of hydrochloric acid is continued two minutes more by way of precaution, after which the porcelain cylinder is filled again with nitrogen or air, and is ready for a determination of density. The platinum tube shown in the plate of the preceding paper is used to introduce the gases, and the capillary tube *c* is exchanged for one with the end bent upwards to disengage the gas under a graduated tube standing in water. The platinum tube must be introduced and withdrawn very slowly to avoid presenting a cold surface to the heated porcelain or the reverse, and at the highest temperatures a vibratory movement must be imparted to it to prevent it from sticking to the porcelain. Although the inside of the cylinder is not enamelled, at temperatures above 1250° the surface appears to be enough softened to attach itself to any object presented, and often pieces of half melted porcelain are found hanging to the tube. A fine platinum wire cannot be withdrawn from the cylinder at this temperature, as it breaks with the force required to overcome its adhesion to the porcelain; it is easily detached when cold however, and at the highest temperatures it is often best to introduce the platinum tube after a series of density determinations have been made and not to withdraw it while the apparatus is hot.

In order to calculate the temperature it is necessary to know the volume V which is heated to the temperature T, and also that of the portion of the stem *b* and the capillary tube *c* which are imperfectly heated. This volume v is heated to a series of unknown temperatures, but their total effect upon the volume of air contained in v may be measured by determining separately the nitrogen which is expelled from a precisely similar apparatus under the same conditions. To effect this we use a compensating tube similar to that described by M. Deville for his air thermometer. In the first experiments at high temperatures we had not been able to procure porcelain tubes closed at one end of precisely the same dimensions as the stems of the cylinders, so that we were obliged to content ourselves with somewhat shorter tubes of Bohemian glass, which penetrated only to the lower surface of the cover of the furnace, so as not to be exposed to a heat that would melt them. We made a series of experiments to assure ourselves that the inner surface of the cover of the furnace marks the boundary between the two volumes V and v, by introducing bits of gold and silver hung from a platinum wire into the stem b and observing the point at which they melted, and we found that the errors in estimating the proportions of V and v in this way were very slight, and subsequent determinations with tubes of porcelain confirmed the results thus obtained. The effect then of the heat upon the volume v which is imperfectly heated is to be ascertained by placing a closed tube of porcelain as nearly as possible beside the stem b of the cylinder, and expelling the air or nitrogen from it with hydrochloric acid as nearly as possible at the same time that the determination of temperature is made with the whole cylinder ab. The capillary tube c and the platinum tube serve for both operations, and it is only necessary to ascertain by a calibration that the capacities of the stem b and the compensating tube are nearly identical and to take into account the variable quantity of air contained in the platinum tube in each operation. The calibration of the total value of air in the whole apparatus abc was usually made by expelling the air at a known temperature (that of the laboratory) with hydrochloric acid, and measuring it in the same graduated tubes used for the other operations; this method is much less troublesome than any other, and has the advantage of rendering the results more easily comparable.

The furnace cover is pierced with two holes for the compensating tube and the stem b, and usually the stream of air which enters the furnace through the ring shaped orifices beside the tubes keeps them from being heated sufficiently to adhere to the furnace cover, but at the very highest temperatures they must be protected with platinum foil.

The following formula is used to calculate the temperature T:

$$T = \frac{V(1 + \beta T) - (A - a)}{(A - a)\,\alpha}$$

$V =$ the capacity in cubic centimetres of the portion of the thermometer which is heated to T degrees.

A = the volume of nitrogen measured at zero which is displaced by hydrochloric acid; consequently A corresponds to the volume of nitrogen heated in $V' + v$.

a = the volume of nitrogen measured at zero which is displaced by hydrochloric acid from the compensating tube; consequently a corresponds to the volume of nitrogen heated in v.

$\alpha = 0.00367$ = the coefficient of expansion of nitrogen under constant pressure.

$\beta = 0.000016$ = the coefficient of expansion of Bayeux porcelain.

An actual experiment may serve as an example.

The porcelain cylinder with the platinum tube and the capillary tube c was found by calibration to contain 98.40 c.c. $= V' + v$, and a similar calibration of the compensating tube with shorter platinum tube and the same capillary tube c gave the volume $v = 6.00 \therefore V' = 92.40$. The volume of nitrogen expelled at the temperature T measured over water at 20.5° (bar. 727.9) was

$$21.45 \therefore \text{A} = \frac{21.45}{1 + 20.5\alpha} \times \frac{709.9}{727.9} = 19.46 \text{ c. c.}$$

The volume of nitrogen expelled from the compensating tube and reduced in the same way was 4.00 c. c.

With these numbers the approximate value of T was calculated, and 1400 substituted for T in the factor $(1 + \beta T) = 1.0225 \therefore V' (1 + \beta T) = 94.47$.

$$T = \frac{94.47 - (19.46 - 4.0)}{(19.46 - 4.0)0.00367} = 1392°.$$

The following experiments were made to control the accuracy of the method. A glass apparatus, of which the portion V' had a capacity of 120.63 c.c., was heated in an iron tube in boiling sulphur, and the air expelled in the manner described. The value of $(1 + \beta T)$ was taken, equal to 1.0149.

I. $A_t = 54.00$ c.c. $t = 18.0.$ bar $= 725.45 \therefore A = 49.58$ c.c.
$a_t = 3.6$ $t = 18.0.$ bar $= 725.45 \therefore a = 3.31$ c.c. $T = 448°$.
II. $A_t = 53.95$ $t = 16.6.$ bar $= 725.45 \therefore A = 49.81$
$a_t = 3.63$ $t = 21.0.$ bar $= 725.40 \therefore a = 3.29$ $T = 445°$.

The true boiling point of sulphur under a barometric pressure of 725 mm. is 445 degrees, so that the second experiment gave an exact result and the first an error of only 3 degrees.

Some determinations were also made of the temperature of a large lead bath using the above apparatus, and immediately afterwards the form of air thermometer with capillary stem proposed by Regnault, in which the thermometer is closed at the temperature *T*, and the diminution of pressure is measured when it is surrounded with ice. These results seemed to be satisfactory, but we do not give them in detail because no means exist of proving that the temperatures compared were absolutely identical as in the preceding experiments.

A series of determinations of temperature made with a porcelain cylinder and compensating tube, heated in the manner indicated in the plate, serves to show approximately the relation between the temperature and the number of litres of gas burned per minute in the large Perrot's furnace. The experiments were only made after several hours' heating had established a constant temperature. It will be seen that the highest limit under these circumstances is about 1370°, and the temperature falls when too much gas is burnt. This phenomenon is still more marked with the smaller furnace.

Litres of gas per minute.	Temperature.	*V.*	*A.*	*a.*
29	1190°	87.31	22 63	6.06
37	1371°	87.31	20.71	5.89
60	1331°	87.21	20.63	5.50
80	1318°	87.21	20.72	5.47
80	1352°	87.21	20.40	5.47

We give here the results of the first determinations of density made before we had recognized the necessity of some of the modifications in the apparatus which were made later, in order that the effect of these changes may be noticed in the subsequent experiments.

The column *D* gives the densities observed; *S* = the weight of iodine; *V* = the volume of air displaced; *t* the temperature of the water in the measuring tube at the moment of reading the volume; *bar* = barometric pressure corrected to zero. The additional columns *D corr.* and *V corr.* give the densities and volumes corrected approximately for the volume of air which enters at the moment that the substance falls to the bottom of the apparatus and before the stopper can be put in its place. This correction varies according to the temperature and the material of the cylinder *d* containing the substance. The first series of density determinations of the vapor of iodine was made by a process as nearly as possible similar to Professor Meyer's, except that the U shaped measuring tube represented in the drawing was employed instead of a measuring cylinder standing over water into which the gas passes through the water.

D	*D* *corr.*	*S*	*V*	*V* *corr.*	*t*	*bar.*	*T*	REMARKS.
8.55	9.20	0.0619	6.10	5.8	17.0	738.8	446.0°	
8.94	9.26	0.1165	11.68	11.28	24.0	735.9	446.0°	Temperature of boiling sulphur.
8.48	8.84	0.0832	8.58	8.23	15.5	723 3	445.0°	
8.62	8.92	0.1195	11.95	11.55	14.2	729.2	445.5°	The true density of vapor of iodine at this temperature is 8.786.
8.68	8.98	0.1268	12.58	12.18	14.2	729.2	445.5°	
8.47	8.81	0.0876	8.93	8.58	14.2	729.0	445.5°	

The preceding experiments were made with a cylinder of which the body *a* was a little more than 20 cm. long and the stem *b* was 7 mm. wide. The variations result chiefly from the difficulty of heating a vessel of this form in boiling sulphur to a perfectly constant temperature.

D	*D* *corr.*	*S*	*V*	*V* *corr.*	*t*	*bar.*	*T*	REMARKS.
8.50	8.80	0.0856	8.86	8.46	17.3	733.4	446.0°	Temperature of boiling sulphur.
8.47	8.75	0.1210	12.41	12.00	17.0	733.0	446.0°	

The cylinder in these last experiments had a wider and shorter body and a narrower stem, and the cylinder *d* containing the iodine was inverted when introduced into the apparatus.

D	*D* *corr.*	*S*	*V*	*V* *corr.*	*t*	*bar.*	*T*	REMARKS.
8.43	8.74	0.1078	10.84	10.46	12 0°	734.1	335.0	Temperature of boiling mercury.
8.31	8.72	0.0833	8.50	8.10	12.0°	734.1	335.0	
8.17	8.73	0.0576	6.24	5.84	19.1°	726.8	394.5°	Temperature of lead bath measured with air thermometer.
8.06	8.69	0.0627	6.79	6.39	19.1°	726.8	394.5	
8.49	8.81	0.1040	10.65	10.25	13.8°	722.5	445.0	Temperature of boiling sulphur.
8.49	8.75	0.1293	13.18	12.78	13.0°	723.0	445.0°	
8.46	8.79	0.1043	10.65	10.25	12.7°	723.0	445.0	
8.44	8.69	0.1340	14.19	13.80	18.0°	716.1	444.5	
8.29	8.75	0.0631	6.70	6.35	17.1°	724.1	508.0	Temperature of lead bath measured with air thermometer.
8.34	8.74	0.0722	7.70	7.35	19.3°	723.7	550.0°	
8.11	8.70	0.0604	6.63	6.18	19.3°	723.7	550.0	

In these last experiments the cylinder *ab* had a capacity of about 130 to 150 c. c., and the interior diameter of the stem *b* was only 3 to 4 mm., and all the precautions which have been recommended were observed except that of closing the apparatus before allowing the substance to fall into the heated cylinder. It may be noticed that the five experiments in which about 0.1 gram of iodine was taken give very concordant results, and the experiments were frequently repeated, because at that time we were unacquainted with the cause of error arising from not closing the apparatus before beginning the experiment, and we believed that iodine actually had an abnormal density at 445°, and wished to multiply experiments in order to confirm so unexpected a result. The correction for the error in question not only gives a nearly normal density for iodine, but also it tends to give identical results with varying quantities of substance, as it should if its application is justifiable.

D	*D* *corr.*	*S*	*V*	*V* *corr.*	*t*	*bar.*	*T*	REMARKS.
*6.48	6.84	0.0991	13.10	12.40	11.5	725.8	590	The substance was weighed in a small pipe-clay cylinder.
*6.45	6.83	0.0997	12.81	12.10	8.8	725.8	610	
7.70	8.33	0.0785	8.98	8.30	18.5	728.5	640	
7.13	7.69	0.0778	9.59	8.90	18.2	728.6	640 650	
7.43	8.00	0.0800	9.47	8.80	19.0	731.0	665	
7.55	8.16	0.0781	9.10	8.40	18.5	731.0		
7.94	8.26	0.0928	10.44	10.04	18.0	716.3	670	The substance was weighed in a very thin cylinder of Bohemian glass.
8.02	8.33	0.0948	10.57	10.17	18.0	716.0		
6.49	6.87	0.0931	12.60	11.90	16.5	724.2	850	The substance was weighed in a pipe-clay cylinder.
6.98	7.32	0.1282	15.51	14.80	11.0	733.7	870	
6.67	7.14	0.0839	10.70	10.00	12.0	731.6	890	
6.53	6.87	0.0963	12.40	11.80	10.0	733.4	1040	The substance was weighed in a platinum cylinder.
5.98	6.55	0.0947	13.57	12.90	21.0	728.2	1040	The substance was weighed in a pipe-clay cylinder.
6.24	6.57	0.0971	13.90	13.20	21.0	727.4	1050	
5.23	5.61	0.0697	11.90	11.10	20.6	725.7	1175	
4.92	5.29	0.0628	11.40	10.60	20.5	725.7	1180	
4.72	5.05	0.0664	11.97	11.20	14.5	739.4	1300	The substance was weighed in a platinum cylinder.

All these last experiments were made with a porcelain cylinder having a capacity of about 100 c. c., and the dimensions indicated in the drawing. The interior diameter of the stem *b* was 7 mm. The smaller Perrot's furnace was used, and the cylinder in the last experiment at 1300° was heated directly in the flame, and in all the others it was enclosed in a piece of stout iron tubing closed at one end. The greater number of the corrected densities at the temperatures below 1000° do not differ greatly from those of the series which follows, and which we regard as exact; but we attach little importance to these results, as we have found no means of

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* We do not know what error causes these results to deviate from the others.

controlling perfectly the value of the correction applied, and we only publish them in the hope that they may afford a clue to at least a part of the differences which appear between determinations made with the apparatus open or closed at the moment of letting fall the substance. It may also be noticed in this connection that the densities in the last series above 1000° approach more nearly a constant number (equal to about two-thirds the normal density) than in the succeeding series, which, as we have already said, gives the true densities of iodine. One of the causes of this result with the last series is, perhaps, the volatilization of a little iodine at the highest temperatures before the stopper is put in its place, and certain peculiarities in the mode of heating, which require further study, may also have contributed to produce the differences between the two series in question.

The following determinations were made exactly in the way which we have recommended in the earlier part of this paper, and we place the results beside those of Professor Meyer* in order to render a comparison easy. The indications of temperature are not strictly comparable on account of the different methods employed to measure them, but we have placed in the same horizontal line the results, which we suppose to have been obtained at nearly the same temperatures, although the highest, which are probably nearly identical, are estimated by Professor Meyer at 1570°, and by us at 1390°. The substance was weighed in a small cylinder of platinum closed with a platinum stopper, so that it can be inverted on introducing it into the apparatus. The use of platinum, which is not at all attacked by iodine under these circumstances, has the advantage of avoiding all possible error that might occur from the disengagement of gas or moisture condensed upon a porous body when a pipe-clay cylinder is used.

VICTOR MEYER.			FR. MEIER and J. M. CRAFTS.				
Temperature.	Density.	$\frac{D'}{D}$					$\frac{D'}{D}$
253°–450°	8.89; 8.83; 8.84; 8.85		1	455		8.70; 8.78; 8.75	
586°	8.73; 8.71; 8.71						
		0.99	2	677—682°		8.06; 8.58	0.94
			3	757°	770—765	8.05; 8.28	0.93
840	6.68; 6.80; 6.80	0.77	4	831—878		8.04; 8.11	0.92
1027	5.75; 5.74		5	1039—1059	1030°	7.18; 7.02; 6.83	0.81
		0.65	6	1270—1280		6.07; 5.57	0.66
1570	5.67; 5.60; 5.71; 5.81	0.65	7	1390°		5.23; 5.31	0.60
			8	1468°		5.06; 5.07	0.58

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* Ber. d. chem. Gesell. 13, 397.

The details of the above determinations of temperature and density are given below.

	T.	*V.*	*A.*	*a.*	*D.*	*S.*	*V.*	*t.*	*bar.*
1	445	*Temperature of Boiling Sulphur.*			8.70	0.1183	11.70	15.2	735.2
	445				8.78	0.1266	12.49	16.0	731.45
	445				8.75	0.1040	10.20	12.9	728.65
2	677	91.94	31.47	4.8	8.06	0.0873	9.43	15.2	726.0
	682	92.04	31.50	4.8	8.58	0.0983	10.00	15.8	726.0
3	757	92.04	29.47	4.8	8.05	0.1110	12.03	16.0	724.9
	770	91.94	29.11	4.8	8.28	0.1138	12.10	16.7	724.9
	765	91.41	29.11	4.8					
4	831	92.60	27.99	4.8	8.04	0.1164	12.49	12.5	724.2
	878	92.60	27.02	4.8	8.11	0.1068	11.44	14.2	723.6
5	1039	91.70	23.93	4.6	7.18	0.1007	12.18	15.0	728.2
	1059	92.60	23.85	4.6	7.02	0.1008	12.46	15.1	728.2
	1030	90.00	23.74	4.6	6.83	0.1004	12.80	16.0	728.2
6	1270	92.53	20.88	4.2	6.07	0.1135	16.58	20.0	729.1
	1280	92.40	20.76	4.2	5.57	0.0908	14.39	18.8	728.75
7	1390	92.25	19.47	4.0	5.23	0.0729	12.46	21.4	727.7
					5.31	0.0727	12.26	21.6	727.6
8	1468	94.80	20.91	5.73	5.06	0.0521	9.07	18.4	727.65
					5.07	0.0636	11.14	19.9	727.65

The large Perrot's furnace was used, and the cylinder protected by an iron tube, was heated in a lead bath weighing 11 kilograms in the determinations up to 878°; between 1000° and 1390° the arrangement of crucibles represented in the drawing was used, and at 1468° the cylinder was covered with platinum foil and was heated directly in the flame. It will be observed that this temperature is higher than could be obtained by heating directly in the flame of the small Perrot's furnace, and it is possible that not only the larger size of the furnace but also the covering of platinum may have contributed to this result. The familiar experiment of placing a porcelain crucible within one of platinum to increase the temperature, suggests that also under the circumstances mentioned the slighter loss of heat by radiation for the metallic surface may enable higher temperatures to be so obtained. It is proposed to make some direct experiments to ascertain this point.

The only source of error that we have been able to discern in this last series of determinations is the too rapid diffusion of iodine or its projection into the stem *b*, from which results a condensation and consequent diminution of the volume of air displaced. This error increases the number representing the density, and we suppose therefore that the lowest densities found are the most exact. We conclude from these experiments that the vapor density of iodine compared with air diminishes *progressively* with the increase of temperature between about 600°, when it is still normal, to about 1470°, where it is only 0.58 of the normal density, and we suppose that a still higher temperature than that which we have thus far been able to obtain would give a half normal density. If this phenomenon is attributed to a dissociation, it must be interpreted to mean that the molecule I_2 is separated into two atoms $I + I$, or else that a group which represents a physical unity is separated into two parts, and we are not disposed to found upon these experiments any new hypotheses regarding the constitution of iodine.

The following table gives the vapor densities of iodine obtained by the essentially different methods employed by MM. Deville and Troost* and by Professor Meyer and ourselves.

Temperature.	Deville and Troost.	Victor Meyer.	Meier and Crafts.
860	8.70	6.75	8.07
1040	8.72	5.75	7.01

The method first proposed by M. Dumas, which was further developed and employed at high temperatures by MM. Deville and Troost, consists in expelling the air from a porcelain bulb by the vapors of a substance heated to a fixed temperature by boiling mercury, sulphur, cadmium or zinc, closing the bulb and comparing the weight of the vapors with that of the air previously contained in it. In the process employed by us the vapors remain mixed with a considerable quantity of air, and it appears probable to Professor Meyer as well as to ourselves that this circumstance may account for a different density in the two cases, supposing that the extent of the dissociation may vary with the tension of vapor, which in our experiments on account of the admixture of air may be one-half, or even less than one-half, that which is attained in the method of MM. Deville and Troost. These authors, however, have published within the last few days a new series† of determinations of the temperatures obtained in the vapors of zinc, which they find to vary according to the mode of heating, and if the new numbers were introduced in the calculation of the density of iodine

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* Annales de Chimie et de Physique, 58, 257.

† Comptes rendus, 90, 773.

together with those obtained in a subsequent determination* of the coefficient of expansion of porcelain, 7.92 would be the density of vapor of iodine at 940°, which is the corrected boiling point of zinc. Our determinations would indicate 7.6–7.7 as the density at that temperature. The new determination of the boiling point of zinc is much nearer that of M. Ed. Bequerel,† who found it to be 930°; he also fixes the boiling point of cadmium at 746.3°, and if this number instead of 860 were employed in calculating the results of MM. Deville and Troost, the vapor density for iodine would be found higher for this temperature than the number we have given. It is not probable that this rectification of the calculations in question is justifiable, because the boiling points were determined with special reference to the modes of heating used in the experiments with iodine, but they at least show that some uncertainties may exist, and that the new determinations which are promised by MM. Deville and Troost may perhaps give lower densities, and consequently bring them more nearly in accordance with ours. We esteem it fortunate that the question will once more be discussed by these chemists, whose determinations have the highest value, since it is they who have established the general methods of operating at high temperatures, and we desire to reserve our opinion upon the differences in our results until these new determinations shall have been made.

In this paper we have discussed some details of the process of Professor Meyer, because we suppose that the divergence of our results may be explained by differences in our modes of operating, but we are far from wishing to criticise in general his excellent method. We can state in a few words our opinion of its usefulness founded upon the experiments thus far made. The new process invented by Professor Meyer is incomparably more convenient than any of those previously in use. As to its exactness, a number of observations were made by one of us upon an organic body which resists extremely well the action of heat, pure benzophenone, and a series of experiments, made immediately after the first publication of Professor Meyer's process, in which his mode of operating was followed exactly, gave excellent results at temperatures between 355° and the beginning of red heat (about 520°). These experiments, undertaken in order to gain familiarity with the method, showed that it requires little practice to distinguish the two phases of the

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* Comptes rendus, 59, 169.

† Annales de Chimie et de Physique, 68, 73.

operation; to reject the first bubbles of air, which are disengaged after putting the stopper in its place, and to collect only those which correspond with the vaporisation of the substance.* It may be added that the rapidity and duration of the disengagement of air afford, after a little experience, valuable evidence regarding the stability of the substance and the sufficiency of the heating above its boiling point. Thus the primitive form of the apparatus, which is simpler than ours, appears to us well adapted to solve nearly all the problems in vapor densities that are presented to a chemist, and we do not consider any modification necessary except in the case when it is required to control other experiments, or where a too rapid volatilization, particularly at high temperatures, renders it impossible to separate the two phases of the operation. On the other hand the resistance of the water which enters the capillary tube in Professor Meyer's apparatus prevents it from indicating small changes of temperature, and this imperfect sensitiveness as a thermometric instrument is sometimes inconvenient.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

VI.—EXPERIMENTS WITH MESITYLENE.

By Lyman B. Hall and Ira Remsen.

The experiments, an account of which will be given in this paper, were begun more than three years ago, and the principal results were soon reached. Many circumstances have interfered, in the meantime, with the prosecution of the work, and even now it will be seen that perfectly satisfactory conclusions have not been reached. There are some points of fundamental importance which remain to be cleared up, but, as the work involved will necessarily occupy considerable time, and we shall be unable to continue it together, it seems best to give a statement of the results thus far reached and to

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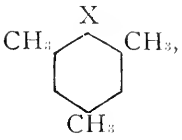
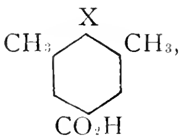
* We have already explained that we attribute the good results under these circumstances to the mutual compensation of two errors, that arising on the one hand from the entrance of air during the falling of the vase *d*, and that arising from the incomplete exit of air through the capillary tube.

indicate the direction in which the research will be continued. The experiments necessary for a complete and final solution of the problem will, it is hoped, be taken up at the beginning of the next academic year, when, as the road is fairly clear, the desired end will probably be attained in a comparatively short space of time.

In the preceding papers of this series the cases studied have been those in which one substituting group is present in an aromatic hydrocarbon containing two oxidizable groups. It has been shown that when the substituting group is in the ortho position with reference to one of the oxidizable groups, the latter is protected from the influence of chromic acid, whereas the other oxidizable group, whether it be in the meta or para position, is converted into carboxyl.

The question would naturally suggest itself: What will be the effect if the substituting group be in the ortho position with reference to two oxidizable groups, and there be, at the same time, a third in the para position? If we take any mono-substitution product of mesitylene, we have in it the conditions mentioned, and represented in this formula, in which X may be any negative atom or acid residue. Now, if it is a general law that all oxidizable residues situated in the ortho position with reference to a substituting group are protected from oxidation, when the compound containing them is treated with chromic acid, whereas oxidizable residues situated in other positions are converted into carboxyl, then the result of oxidizing a compound of the formula given above would be an acid of this formula, which is plainly monobasic.





In order to test the question here involved, the sulphamide of mesitylene was first selected.

Oxidation of Mesitylenesulphamide with Chromic Acid.

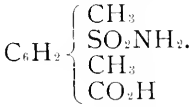
The sulphamide of mesitylene was prepared from pure mesitylene by means of the usual reactions and then purified by recrystallization from water. It was treated with the oxidizing agent in the following proportions: 2 grams amide, 14 grams potassium pyrochromate, 20 grams concentrated sulphuric acid diluted with three times its volume of water. The mixture was boiled in a flask connected with an inverted condenser. The amide gradually passed into solution and the oxidizing mixture changed its color. After boiling for about five hours, a crystallized substance began to separate from the solution while still hot. On cooling, the quantity of this product increased, and corresponded then very closely to the quantity of the amide taken for oxidation. It was filtered off and well washed with cold water, when there remained upon the filter a pure white crystallized substance. The new product was separated from some of the oxidized amide which was still mixed with it by treating it with a cold solution of sodium carbonate. It dissolved very readily, an evolution of carbon dioxide taking place at the same time, while the unoxidized amide remained undissolved. On adding hydrochloric acid to the filtered solution a voluminous crystalline precipitate was formed. This was recrystallized from water two or three times, and then exhibited the properties of a chemically pure substance. The analyses gave the following results:

I. 0.27955 gram gave 0.5306 gram CO_2 and 0.1117 gram H_2O.
II. 0.23275 gram gave 0.4404 gram CO_2 and 0.1066 gram H_2O.
III. 0.26775 gram gave 0.5063 gram CO_2 and 0.117 gram H_2O.
IV. 0.21285 gram gave 0.4024 gram CO_2 and 0.088 gram H_2O.

Analyses 1 and 4 were made with copper oxide; 2 and 3 were made with lead chromate and a mixture of potassium chromate and pyrochromate.

V. 0.3498 gram gave 0.3831 gram $BaSO_4$.
VI. 0.3647 gram gave 0.4006 gram $BaSO_4$.

According to the analyses the mean percentage of carbon is 51.64, that of hydrogen 4.73, and of sulphur 15.05. These results do not correspond to any simple oxidation product of the original sulphamide. The simplest product imaginable, and the one the formation of which was expected, is sulphaminemesitylenic acid,



$$C_6H_2\begin{cases}CH_3\\SO_2NH_2.\\CH_3\\CO_2H\end{cases}$$

But a substance of this formula requires 47.16 per cent. carbon, 4.8 per cent. hydrogen, and 13.97 per cent. sulphur, and these figures can certainly not be brought in harmony with those found. On the other hand the results found correspond fairly well with those required by a substance differing from sulphaminemesitylenic acid by containing one molecule of water less, and bearing the same relation to the acid that the sulphinides described in earlier papers bear to the corresponding acids. The simplest example of this kind of compounds is benzoic sulphinide, $C_6H_4 \left\{ \begin{matrix} CO \\ SO_2 \end{matrix} \right\} NH$. The substance under consideration would, according to the principle of nomenclature previously adopted, receive the name *mesitylenic sulphinide*, and its formula is $C_6H_2 \left\{ \begin{matrix} (CH_3)_2 \\ SO_2NH. \\ CO \end{matrix} \right.$ In the table here given the results of the analyses are placed side by side with those required for mesitylenic sulphinide.

Calculated for $C_6H_2 \left\{ \begin{matrix} (CH_3)_2 \\ SO_2NH. \\ CO \end{matrix} \right.$			Found.					
			I.	II.	III.	IV.	V.	VI.
C_9	108	51.18	51.76	51.62	51.54	51.53		
H_9	9	4.27	4.43	5.07	4.8	4.6		
S	32	15.16	...	...	...	...	15.02	15.08
N	14	6.64	...	...	...	...	...	...
O_3	48	22.75	...	...	...	...	...	...
	211	100.00						

The results do not agree as closely with those required for the formula as could be desired, but when the difficulty of effecting a satisfactory combustion of a substance containing carbon, hydrogen, oxygen, sulphur and nitrogen is taken into consideration, it will, we believe, be acknowledged that the formula proposed and accepted by us is established by our analyses.

Mesitylenic sulphinide, $C_6H_2 \left\{ \begin{matrix} (CH_3)_2 \\ SO_2NH, \\ CO \end{matrix} \right.$ is almost insoluble in cold water and with difficulty in boiling water. It is easily soluble in alcohol and ether. From any one of these solvents it may be obtained in crystallized form, though it is best purified by crystallization from water from which it is deposited in the form of short, thick, somewhat irregularly formed, lustrous prisms. It fuses at 255° uncorrected and 262° (corrected).* Like the sulphinides which have already been examined, this one when treated in aqueous solution with carbonates furnishes salts of the corresponding acid.

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*Jacobsen (Ber. deutsch. chem. Gesell. 12, 604), who has since prepared this substance, gives the fusing point 259° (corrected 263°).

Calcium sulphaminemesitylenate, $[C_6H_2.(CH_3)_2.SO_2NH_2.COO]_2Ca + 6H_2O$, was prepared by boiling mesitylenic sulphinide and finely powdered Iceland spar together in water. It is easily soluble in water and crystallizes in long, flat, transparent plates. It is also soluble in alcohol.

0.28685 gram lost 0.0523 gram H_2O at 195°, and gave 0.06865 $CaSO_4$.

	Calculated.		Found.
$(C_9H_{10}SNO_4)_2$	456	75.50	...
Ca	40	6.62	7.03
$6H_2O$	108	17.88	18.05
	604	100.00	

The *barium salt* is very easily soluble. It crystallizes in groups of very delicate lustrous needles.

Copper sulphaminemesitylenate, $[C_6H_4(CH_3)_2.SO_2NH_2.COO]_2Cu+4H_2O$. This is the most characteristic salt of the acid examined by us. It was prepared by precipitating a solution of the barium salt with copper sulphate. It consists of beautiful, bright blue, small needles which radiate from a centre and thus form groups. These crystals lose water over sulphuric acid after they have been perfectly dried in the air. Placed again in the air, they take up the water rapidly. If, however, all the water of crystallization is driven off by heating to 200° the anhydrous crystals do not take up water by contact with the air. The anhydrous salt has a bright green color. The analyses yielded the following results:

I. 0.2358 gram dried in the air lost 0.0293 gram H_2O at 200° and gave 0.0325 gram CuO.

II. 0.3473 gram dried in the air lost 0.043 gram H_2O at 200° and gave 0.0482 gram CuO.

	Calculated.		Found.	
			I.	II.
$(C_9H_{10}SNO_4)_2$	456.	77.11	...	...
Cu	63.4	10.72	11.01	10.79
$4H_2O$	72.	12.17	12.42	12.38
	591.4	100.00		

Jacobsen* states that this salt contains only three molecules of

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* Loc. cit.

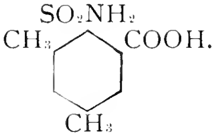
water of crystallization. He has not, however, as yet communicated his analytical data.

The *silver salt* was prepared by adding a solution of silver nitrate to a dilute, neutral solution of the ammonium salt. It was at once thrown down as a heavy white precipitate, which could be dissolved in water only with difficulty. This precipitate was filtered off and washed until no trace of nitric acid could be detected, and, after drying in the air, it was analyzed. Heated up to 160°, its weight remained constant.

I. 0.203 gram salt gave 0.0685 gram Ag.
II. 0.2303 gram salt gave 0.07815 gram Ag.
III. 0.322 gram salt gave 0.1088 gram Ag.

These results correspond respectively to 33.74, 33.93, and 33.78 per cent. silver, or a mean of 33.81 per cent. The formula, $C_6H_2SO_2NH_2(CH_3)_2COOAg$, requires only 32.14 per cent., so that we find an excess of 1.67 per cent. It is difficult to account for this, as every precaution was taken to insure purity of the salt. It is curious that the results found correspond to that required by a salt containing a molecule of water less than silver sulphaminemesitylenate. It is barely possible that the precipitate formed is a compound of the formula $C_6H_2\begin{cases}(CH_3)_2\\ \left.\begin{array}{l}SO_2NAg,\\ CO\end{array}\right]\end{cases}$ or the sulphinide in which the hydrogen atom of the imide group is replaced by an atom of silver. This would require 33.96 per cent. silver, a figure which agrees very well with the 33.81 per cent. found. Improbable as this supposition may appear, it is not entirely without analogy, as it is known that the amides of some of the aromatic sulphonic acids furnish silver compounds in which the silver is situated in the ammonia residue.

It is thus shown at least that when mesitylenesulphamide is treated with chromic acid only one of the methyl groups is oxidized, while the other two remain unchanged. The conclusion which would naturally be drawn from this fact, if the results obtained in other similar cases be taken into account, is that the para methyl group is the one that has been changed, the other groups being protected. On the other hand, as it has been shown that the kind of combination characteristic of the sulphinides is found in compounds in which the SO_2NH_2 group and the COOH are in the ortho position with reference to each other, and has not been observed in other cases, we would be led to believe that mesitylenic sulphinide is derived from orthosulphaminemesitylenic acid, According to this it is an ortho methyl group which is oxidized, and not the para group, as was supposed. The question remains, as far as our results are concerned, an open one. In the concluding part of this paper this subject will be discussed more fully, and some other facts bearing upon it will then receive consideration.



Formation of a Bibasic Acid from Mesitylenesulphamide.

When the chromic acid oxidizing mixture from which mesitylenic sulphinide has been separated is allowed to stand for a time, or is concentrated by evaporation on a water-bath, a second product is obtained in small quantity. This was separated from the mixture and purified by crystallization. It crystallizes well from water in the form of large transparent plates, grouped together in bunches. It is more easily soluble in water, alcohol and ether than the sulphinide. It fuses at 279°. It was found to be a strong acid, and some of its salts were prepared and analyzed. Although the results of the analyses do not agree well for any probable formula, the amount of barium found in the barium salt showed clearly that the substance is a bibasic acid. Then, further, the acid was heated in a sealed tube with concentrated hydrochloric acid at 230°, and a product obtained which corresponds very closely to uvitic acid. It is much more difficultly soluble than the original acid, and separates from the solution, on cooling, in the form of fine needles, which fuse well at 288–289°. There can be little doubt that the acid with these properties is uvitic acid, and it follows that the new product is either sulphamineuvitic acid or the corresponding sulphinide.

It is hence evident that, when mesitylenesulphamide is treated with chromic acid, two methyl groups, one of which must be situated in the ortho position with reference to the sulphamide group, are oxidized. But it is an important fact that *only a very small quantity of the bibasic acid is formed.* These results suggest those obtained in connection with the sulphamides of meta- and paraxylene. It will be remembered that *very small quantities* of bibasic acids were also obtained from these compounds.

In order to obtain the bibasic acid in larger quantity, the sulphamide was treated with potassium permanganate in excess. The acid was readily obtained, and, under the conditions of our first experiments, it was the sole product of the oxidation. If the permanganate solution be added gradually to the solution of the sulphamide the results are different, as Jacobsen* has recently found; and later experiments of our own confirm, in this respect, the results obtained by him. We have also found that, when larger quantities of the sulphamide are subjected to oxidation with the permanganate, there is formed some of the sulphinide, and, on evaporating the filtrate from the manganese hydroxides, there are thrown down on the addition of hydrochloric acid three substances: (1) the bibasic acid fusing at 279°; (2) mesitylenic sulphinide; and (3), if the hydrochloric acid be not too concentrated, the acid potassium salt of the bibasic acid.

The free acid was converted into the barium salt by boiling it with barium carbonate in water. It is easily soluble in water, and could not be prepared in crystallized form. When once separated from the aqueous solution, it dissolves with difficulty. It contains water of crystallization, which it gives up partially in contact with the air. The salt obtained by oxidation with permanganate was analyzed with the following results:

I. 0.3857 gram lost 0.046 gram H_2O at 290°, and gave 0.1999 gram $BaSO_4$.

II. 0.3065 gram lost 0.0369 gram H_2O at 290°, and gave 0.1588 gram $BaSO_4$.

	Calculated.		Found.	
			I.	II.
$C_9H_7SNO_6$	257	57.37	...	...
Ba	137	30.58	30.47	30.46
$3H_2O$	54	12.05	11.93	12.03
	448			

The results agree with those required for the formula $C_6H_2.CH_3.SO_2NH_2.(COO)_2Ba + 3H_2O$, or the acid from which it is derived is sulphamineuvitic acid.

By fusing the acid with potassium hydroxide a new substance was obtained, which has in general the properties of the oxy-acids. It is very difficultly soluble in hot water, and practically insoluble in cold water. It fuses at 294–295°. It separates from a hot aqueous solution in very small compact crystals. It is easily soluble in alcohol and ether, and insoluble in chloroform. Its solution

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* Ber. deutsch. chem. Gesell. 12, 604.

is colored red by ferric chloride; the color is, however, not strong, and as we have no good guarantee that our acid was perfectly pure, it may be that this coloration is due to the presence in small quantity of some other oxy-compound.

The *barium salt* of the oxy-acid was obtained in the form of a peculiar looking, gelatinous mass, easily soluble in water.

The *calcium salt* forms delicate, interlacing needles, which have a slight brown color. This salt was analyzed, and the results agree moderately well with those required for the calcium salt of *oxyuvitic acid.*

I. 0.1317 gram salt lost 0.0321 gram H_2O at 200°, and gave 0.0566 gram $CaSO_4$.

II. 0.165 gram salt lost 0.0409 gram H_2O at 200°, and gave 0.0705 gram $CaSO_4$.

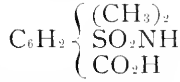
Calculated.					Found.	
					I.	II.
$C_9H_6O_5$	...	194	...	...	...	...
Ca	...	40	...	13.07	12.63	12.56
$4H_2O$	...	72	...	23.53	24.37	24.78
		306		100.00		

The results for the water of crystallization agree very poorly with those required by the formula. Calculating the results for calcium on the basis of the anhydrous salt, the amount required is 17.10 per cent., while the results obtained correspond to 16.71 and 16.70 per cent. respectively.

The sulphamineuvitic acid first obtained was formed by the oxidation of the *sulphamide* with potassium pyrochromate or potassium permanganate. The *sulphinide* was now subjected in turn to the action of each of these oxidizing agents. A marked difference was observed in the two cases. The permanganate readily converts the sulphinide into the bibasic acid, the yield being very good. This method appears, indeed, to be the best one for the preparation of the new acid. On the other hand, pure *mesitylenic sulphinide may be boiled with the usual chromic acid mixture for days without undergoing material change.* In one experiment performed with a weighed quantity of the sulphinide the boiling was continued for four days. Almost the entire quantity taken of the original substance was recovered, and only a trace of the bibasic acid could be detected.

Thus far we have been unable to detect a tribasic acid among the products of oxidation of mesitylenesulphamide or mesitylenic sulphinide. The bibasic acid is readily formed, as has been shown, both from the sulphamide and the sulphinide. Whether the bibasic acid obtained by us under different conditions always represented the same compound or not, is a question which we cannot as yet positively answer. The free acid (or sulphinide) had always very nearly the same fusing point, and presented very nearly the same appearance, but there were slight differences observed between the products obtained at different times, which suggested the possibility at least that these products might be isomeric and not identical.

Formation of a Sulphaminemesitylenic Acid.

In a paper published two years after the first results of this investigation had appeared in print, Jacobsen* describes a new product of the oxidation of mesitylenesulphamide with potassium permanganate. This is a substance of the formula,  $C_6H_2\left\{\begin{array}{l}(CH_3)_2\\ SO_2NH_2\\ CO_2H\end{array}\right.$, to which is given the name *parasulphaminemesitylenic acid.* This acid was obtained, together with the isomeric ortho-acid, by oxidizing the sulphamide with permanganate. Jacobsen states that a mixture of the two acids is formed, and says nothing concerning the bibasic acid. We have repeated his experiments, and obtained three products: (1) mesitylenic sulphinide (according to Jacobsen orthosulphomesitylenic acid); (2) parasulphaminemesitylenic acid; and (3) the acid potassium salt of the bibasic acid. The formation of the last product was evidently not noticed by Jacobsen. It is possible, of course, that it may not have been formed in his experiments, but it was certainly always formed in ours. As regards the sulphaminemesitylenic acid, a substance corresponding to the one described by Jacobsen under this name was obtained by us. It crystallizes in needles, and fuses at 270° (uncorr.) and 276° (corr.). It was not fully analyzed, but two sulphur estimations which were made gave results corresponding to the formula of sulphaminemesitylenic acid.

I. 0.2995 gram acid gave 0.3044 gram $BaSO_4$.
II. 0.2222 gram acid gave 0.2214 gram $BaSO_4$.

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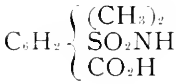
* Ber. deutsch. chem. Gesell. 12, 604.

The formula 

$$C_6H_2\begin{cases}(CH_3)_2\\ SO_2NH_2\\ CO_2H\end{cases}$$

requires 13.97 per cent. sulphur, while the above results correspond respectively to 13.95 and 13.68 per cent. sulphur.

Structure of the Oxidation Products from Mesitylenesulphamide.

In order to learn more in regard to the nature of mesitylenic sulphinide it was fused with potassium hydroxide in the hope that it would be converted into an oxymesitylenic acid. A considerable quantity of the substance was thus fused and the resulting mass treated in the usual manner. The product is a white crystallized acid possessing all the properties of mesitylenic acid. It is volatile with water vapor. It fuses at 166–167°. It is not colored by ferric chloride. Its solubility corresponds to that of mesitylenic acid. All the solutions were carefully examined for oxymesitylenic acid, but only a slightly bluish tint was produced by ferric chloride, even in the last mother-liquor. It is hence exceedingly doubtful whether even a trace of this acid was formed.

From the pure mesitylenic acid the silver salt was prepared. It was found to contain a molecule of water of crystallization, a fact not stated by Fittig* in his paper on mesitylenic acid.

I. 0.13745 gram of the air-dried salt lost 0.00875 gram H_2O at 100°, and gave 0.054 gram Ag.

II. 0.31945 gram salt lost 0.02125 gram H_2O at 100°, and gave 0.125 gram Ag.

	Calculated.			Found.	
				I.	II.
$C_9H_9O_2$	149	54.19	...	...	...
Ag	108	39.26	...	39.28	39.13
H_2O	18	6.54	...	6.37	6.65
	275	100.00			

The action of fusing potassium hydroxide causes then simply a replacement of the sulphamine group by hydrogen. Some similar cases have previously been observed, among which may be mentioned the formation of salicylic acid by fusing sulphosalicylic acid with potassium hydroxide,† and the formation of oxybenzoic acid from a sulpho-derivative of oxybenzoic acid of unknown composi-

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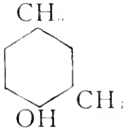
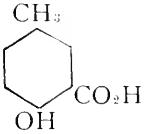
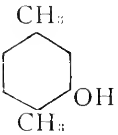
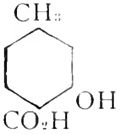
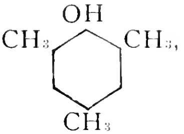
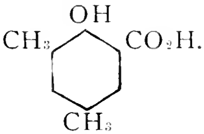
*Annalen der Chemie, 141, 148.

† Remsen. Ibid. 179, 107.

tion.* The conditions which cause this apparently abnormal action are not clear.

Jacobsen has recently also made the above observation. He has further shown that, when his parasulphaminemesitylenic acid is fused with potassium hydroxide, it is converted into an oxy-acid isomeric with oxymesitylenic acid. If now we can determine the structure of either of the oxymesitylenic acids, that of the corresponding sulphamine derivatives would be given. In regard to ordinary oxymesitylenic acid one of us (R) has already called attention† to the fact that its structure can be deduced with a fair degree of probability from its mode of formation, by fusion of mesitylenesulphonic acid with potassium hydroxide. The proof is as follows:

By fusing liquid metaxylenol  with potassium hydroxide Jacobsen obtained‡ an oxytoluic acid of the formula , and from paraxylenol  he obtained§ an acid . Similar results were obtained by fusing thymol and carvacrol—the oxidation took place in the ortho-group. Accordingly, by fusing mesitylenesulphonic acid with alkali, we would expect the formation, first of the oxy-derivative , and, if the principle indicated in the experiments of Jacobsen is a general one, the formula of oxymesitylenic acid must be .

The properties of the acid are in harmony with this view. It is volatile with water vapor and gives a color reaction with ferric

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* Smith. Journ. pr. Chem. N.F. 16, 231.

† Ber. deutsch. chem. Gesell. 11, 2091.

‡ Ibid. 11, 375.

§ Ibid. 11, 570.

chloride, and the investigations of Tiemann have made it very probable that among the aromatic oxy-acids only those which are derived from salicylic acid possess these two properties. The above formula represents oxymesitylenic acid as a derivative of salicylic acid, whereas, if the acid possessed the other possible structure, it would be a derivative of paraoxybenzoic acid.

After the publication of the above reasoning concerning oxymesitylenic acid, Jacobsen* furnished the experimental proof of the correctness of the view, first expressed by us, by heating the acid with concentrated hydrochloric acid at a high temperature. Under these circumstances carbon dioxide is split off and the corresponding xylenol obtained. The latter was then identified with the 1. 3. 4. xylenol.

Now it would follow, from the fact that parasulphaminemesitylenic acid is converted into an oxymesitylenic acid isomeric with the ordinary variety, that, in the new oxymesitylenic acid, as well as parasulphaminemesitylenic acid, the substituting groups are in the para-position with reference to the carboxyl, and, further, in mesitylenic sulphinide, the residues of the carboxyl and the sulphamine groups are in the ortho-position.

The conclusion to which we are at present forced is, hence, the opposite of that which we anticipated, and, if future experiments should confirm the conclusion, it would appear that, in some cases, there must be other conditions than the position of the substituting group which determine the character of the oxidation. That the position of the groups with reference to each other, or, at least, that something which we at present designate as position, influences very markedly in many cases the character of the oxidation, is clear from many facts known to us, prominent among which may be mentioned those described in the earlier papers of this series. But if position is the only condition governing the process, then, from our previous experiments, it would seem to follow, as a necessary consequence, that when mesitylenesulphamide is oxidized with chromic acid, the two ortho-methyl groups should be protected and the para group oxidized. According to the evidence thus far in our possession, this does not take place.

Before accepting the above evidence as final, it is proposed to repeat on a larger scale some experiments which we have already performed, and which seem to lead to a different conclusion from that above referred to.

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* Annalen der Chemie, 195. 279.

In order to determine the structure of mesitylenic sulphinide we went to work in the manner here described: Mesitylenic acid was converted into sulphonic acids. Two were formed, and these can be separated comparatively readily through the barium salts. Both barium salts were converted into the potassium salts. For the present let us call these the α and β salts.

The α salt, treated with phosphorus pentachloride and ammonia, yields an amide which crystallizes in long white needles, and does not fuse at 300°. The same salt, when fused with potassium hydroxide, yields oxymesitylenic acid with all its characteristic properties.

The β salt yields an amide fusing at about 287°; and with potassa an acid fusing at 223°. This latter substance is, in all probability, the parasulphaminemesitylenic acid.

Now, by treating mesitylenic sulphinide with phosphorus pentachloride and ammonia, a substance was obtained which fuses at 287°. According to this, the sulphinide belongs in the same group with the β salt; and, as this salt yields parasulphaminemesitylenic acid, the sulphinide itself would be a para-compound. These last experiments can, however, be regarded only as preliminary, and they are only mentioned now in order to indicate the direction in which the investigation will be continued.

MAY, 1880.

REVIEWS AND REPORTS.

BRIEF REVIEW OF THE MOST IMPORTANT CHANGES IN THE INDUSTRIAL APPLICATIONS OF CHEMISTRY WITHIN THE LAST FEW YEARS.

(Continued from Vol. II, p. 67.)

MATERIALS USED AS FOOD.

Bread.—Probably the most valuable aid has been rendered to bread-making by the careful manufacture on a greatly increased scale of pressed yeast, which improved means of rapid transportation have permitted to be sent in still fresh and sound condition to an ever enlarging circle of consumers. In this country, more than elsewhere, the use of various "baking powders" prevails, intended to produce carbon dioxide throughout the mass of dough, thus rendering it spongy. Of these preparations two require mention beside the long used cream of tartar and bicarbonate of soda; namely, the acid calcium phosphate (with same alkaline carbonate and a little potassium chloride) of Horsford, now largely and advantageously employed, and the dried ammonium alum with sodium carbonate which has for the last few years been extensively sold, but with very doubtful advantage on the score of wholesomeness.

Meat.—In view of the conditions under which the animals most used for food must be reared, most cheaply at great distances from the dense population by which they will chiefly be consumed, one of the most important of modern industrial problems is that of meat preservation. On the whole, the first place among the many recent attempts at a satisfactory solution may fairly be given to the process of "canning,"—exposure of the meat in suitable vessels, practically cylinders of tin-plate, to a temperature high enough to destroy the vitality of organized ferments, and to expel most of the air from the unoccupied part of the vessel, followed by effectual exclusion of the atmosphere by sealing hermetically with solder. The method may be called recent, since, although fully worked out by Appert as early as 1796–1804, it remained but little used until some fifteen or twenty years ago as compared with its great extension at the present day. It is needless to say that this process is also most useful in its application to fish, milk, vegetables and other forms of perishable food.

Another mode of preserving meat in fit condition for use, excellent in its results, but formerly difficult to carry out in practice, namely, the maintenance of the flesh at a temperature not much above the freezing point, has been brought much more under control by the numerous machines for the production of artificial cold. Although success has attended this plan as applied both for sea and land transportation, the latter commonly with the aid of natural ice, it doubtless admits of being developed upon a larger scale in the future.

Of lately introduced chemical agents to be used as preservatives the most prominent have been salicylic acid and boracic acid or soluble borates. The former, economically manufactured from phenol by Kolbe's synthetic process, is an efficient antiseptic, but limited in its application to meat by its disagreeable taste and the irritant effect it produces upon the fauces when used in needful quantity. The tastelessness of boracic acid, and of the acid phosphates, whose production by its means is, according to Endemann, the chief source of its utility, constitutes an advantage in its favor, but the question of possible danger to health from long continued ingestion of boracic acid or its salts cannot be said to have yet been satisfactorily settled.

Meat Extracts.—Beside the use upon a much larger scale than formerly of meat extract made by Liebig's original process, the introduction is to be noted of analogous products differing therefrom in retaining the animal albumen in uncoagulated form, the evaporation being carried out at temperatures never allowed to reach 60° C. Valentine's "meat juice" represents one of the most carefully prepared of these materials. The process of Leube, published some years ago, involves still another idea, that of bringing into solution the whole of the albumenoids, including the solid muscular fibre, by digestion of the lean meat under pressure with water containing a little hydrochloric acid, neutralizing the free acid with sodium carbonate, and evaporating cautiously to extract consistence. This plan does not seem to have come into general use, nor has any definite reason been given for the failure to employ it.

Preserved Vegetables.—The extensive application of the Appert system of "canning" to fresh vegetable food, tomatoes, peas, young Indian corn, and the like, has been supplemented by the process of desiccation, admirably carried out by Chollet & C$^{ie.}$ of Paris, among other firms. The vegetables to be thus preserved are exposed for a short time to the action of steam under considerably more than normal pressure, then rapidly dried in a current of warm air, and finally pressed hard into cakes under a hydraulic press. As an addition to a soldier's ration, these cakes deserve attention from their wholesomeness, the very fair degree in which the fresh odor and flavor are retained for a considerable time, and the convenient form presented for transportation. The now celebrated *Erbswurst* of the Franco-Prussian war involves the principle of desiccation along with that of admixture with fat, but is chiefly noteworthy on the ground of its supplying albumenoid food from a vegetable source and in concentrated and portable form. Desiccation alone has also been usefully applied to eggs, the yolks and whites of which, carefully dried at a low temperature, can long be preserved in fit state for use in cooking.

Butter and Cheese.—The manufacture of these milk products has, notably in some parts of the United States, tended of late years to pass from domestic hands, as a simple farm industry, into those of firms occupied exclusively with dairy operations, the work being carried on in large factories, fitted up with special plant, and supplied with engine power. The minute details of the manufacture, exact attention to temperature, exclusion of ferments, etc., are looked to with much more care in such establishments than they can well be in private hands.

The "artificial butter," "oleo-margarine," or prepared beef fat of Mouriès, has come into use on a very large scale, and, notwithstanding the prejudice aroused against it by its fraudulent sale as actual butter, it must be counted as a not unwholesome, and under some circumstances a valuable addition to the food resources of the world, it being assumed of course that the manufacture itself is honestly carried out with sound material to work upon.

Sugar.—This important manufacture has in its various stages undergone sundry modifications. In some of the regions of production, both from the juice of the cane and from that of the beet, there has been an extension of the practice of making a more or less refined product directly from the crude material, but in general the tendency has been rather in the opposite direction, to a distinct separation of the business of making raw sugar by simple means from the juice, and that of refining this raw sugar for the superior purposes of consumption. Even further subdivision of the industry is largely practised; many producers of beet-roots confining themselves to rasping them to pulp and pressing out the juice, to be sold at a stipulated rate to the sugar-makers proper, and sent to them by means of underground pipes, hundreds of miles of which on the Linard system have been laid in Northern France and in Belgium; while, at the other end of the process of manufacture, the working up of molasses and refinery syrups is often found in other hands than those of the first makers of crystallized sugar with whom they have originated.

The success and actual distribution of the sugar industry in different parts of the world, in whatever form conducted, has varied much from time to time, as in the case of Russia, where the extension of production from beet-root has been wonderfully rapid, and in Austria, where the same industry has notably fallen off; everywhere the influence of tariff and internal revenue legislation has had much to do with modifying the effects of natural conditions and of the progress due to improved methods of production.

In obtaining the juice from beet-root the older use of hydraulic presses has been largely suspurseded by the more modern cylinder presses, and of late the horizontal direct-acting filter presses have been used with advantage, both as to the amount of juice obtained and its degree of freedom from fine fragments of vegetable fibre.

The diffusion process, by which thin slices of the fresh root are exhausted of sugar by successive portions of water, has become firmly established in many factories, avoiding the use of costly machinery and much engine power, furnishing a purer juice than that obtained by expression, and in consequence of the systematic use of the water in the successive cylinders of the diffusion battery not seriously increasing the consumption of fuel for evaporation. It is much to be desired that the same process should be generally extended to the extraction of juice from the sugar cane; the feasibility of this having been fairly established by experiments on the full working scale with the apparatus of Robert; no other method seems so likely to remedy the enormous loss of juice, fully one-third of the whole, now experienced in the ordinary mill crushing.

For the purpose of rapidly reducing cane juice by evaporation to the condition of a solid mass, capable of being kept without material alteration and shipped to distant points for manufacture into saleable sugar in the hands of the refiner, the simple and effective apparatus known as Fryer's concretor deserves special attention; already considerable quantities of "concrete" made with it have been shipped from West Indian and South American ports with satisfactory results, both to the sugar planter and refiner.

In the clarification of the juice from beet-root the chief recent modification has been the use of largely increased quantities of lime, to be afterwards removed by a current of carbon dioxide gas as usual, the much larger amount of scums and sediment thus produced proving manageable with the aid of the improved filter presses; saving of bone-black in the subsequent filtration may thus be effected.

The kilns for charring and revivifying the bone-black used in the decolorizing filters have been improved in various points of detail as to construction, method of working, and durability. Decolorization by bone-black has come more frequently into use on plantations making white sugar directly from cane juice, as in some districts in Cuba.

The vacuum pan for evaporation of the juice is also more often to be seen as a portion of the equipment of plantation sugar-houses. In boiling down the juice, whether of cane or beet, the practice has become more common of crystallizing much of the sugar in the vacuum pan itself before transference of the mass to the coolers.

In regard to the crystallization and drainage, although the old fashioned loaf sugar is still made, loose crystals drained and washed in the centrifugal machine have assumed much greater importance, and the former practice of crushing or cutting up loaf sugar into fragments of convenient size to be used in tea, coffee, etc., has been reversed, lumps being now moulded by pressure from loose granular sugar in fine crystals.

In recovering an additional amount of crystallizable sugar from the molasses of first drainage the process of most importance is that of dialysis through parchment paper, to recover much saline matter by osmose before a second crystallization, as originally proposed by Dubrunfaut. The liquid from the water cells of the dialyzer is either fermented and distilled to recover such small amount of sugar as it contains, or is simply evaporated to dryness and the saline residue utilized as manure. Less in use than this, but yet practically employed by a good many factories, is the process for separation of sugar from molasses as sugar lime, washing with alcohol.

In the distinct industry of making starch sugar, the consumption of which by brewers, manufacturers of factitious wines, table syrups and caramel, and in the adulteration of the cheaper grades of brown sugar, has assumed very large proportions, less water is used than formerly and very little acid, but the process is conducted in close vessels under pressure sufficient to allow of the temperature rising to as much as 160° C. The product is to be found in the form of a granulated crystalline mass, in solid blocks, and as a thick, highly viscid syrup, the last containing much dextrine.

Wine.—The manufacture of this, as of all other alcoholic beverages, has been placed upon a more rational basis by the valuable researches on fermentation of Pasteur, Liebig, Rees, Brefeld and others.

Chemical materials have been employed to combat the diseases of the grape-vine in Europe due to fungoid and insect attacks. It seems still doubtful whether the former of these two sources of injury is capable of being reached by sulphur itself, or only by the acid products of its oxidation; if the latter be the case there is enormous waste of material in the flowers of sulphur actually in use.

The most distinctly novel step in modern wine-making itself is doubtless Pasteur's process for destroying organized ferments in the bottles or other close vessels used to finally contain the wine, by heating for half an hour or an hour to 60° or 70° C. Valuable as is this process in principle, it requires care in practically carrying it out, and its use has been restricted in France by the liability to injure the delicate *bouquet* of the finer wines in applying this method to their preservation.

Much so-called chemical skill is ill bestowed upon the fraudulent practice of wine fabrication and adulteration, although it is perhaps more difficult in regard to this than to most other industries to draw the line between adulteration and legitimate variations of ordinary practice, as for instance the use of clarifying materials and special forms of tannin, the employment of plaster in the vats, etc.

Beer.—As an addition to wort made from simple malt, glucose and dextrine made from starch by boiling with dilute acid have come into extensive use.

O'Sullivan and Valentine have introduced an analogous material containing maltose instead of glucose, made by the action of dilute sulphuric acid upon ground rice under carefully regulated conditions of time and temperature, the solution obtained being neutralized with chalk, filtered and evaporated in the vacuum pan to a cake consisting of two-thirds maltose and one-third dextrine. Glycerine is also very largely employed as an addition to the wort, serving to sweeten and give consistence to the beer and to moderate in some degree the fermentation.

In boiling the wort hop-extracts have of late to some extent taken the place of actual hops. It is said that these extracts are often made with light petroleum naphtha as the original solvent.

Pasteur has applied his views of fermentation to the proper cooling of the wort by proposing that, immediately after boiling, it be run off into close vessels, and that in these it be kept covered by a stratum of carbon dioxide drawn from the fermenting vats until it has been cooled down to proper temperature, yeast added and fermentation fairly set up. In the rapid cooling of the wort when contact with the air is not cut off, advantage has been taken of the modern ice machines to produce the required reduction of temperature; some of the forms of such machines less adapted to the actual production of ice, as that worked with air alternately compressed and expanded, answering very well for this purpose, with its moderate cooling of very large masses of liquid.

As affording the means of regulating the fermentation, by the addition of a very small quantity of foreign material without objectionable effect upon the taste of the beverage, salicylic acid has been proposed by Kolbe and to some extent used.

Pasteur's heating process has been found equally effective for the preservation of bottled beer, such as is largely sent to warm climates, as for that of wine.

Distilled Spirits.—The manufacture of spirit from potatoes has undergone great expansion, especially in Central Europe, while the increase of beet-root production has in various countries, particularly in France, led to a corresponding increase in the distillation of alcohol from the residual molasses.

In making potato spirit the practice has been introduced of rapidly steaming the potatoes under increased pressure, then reducing the pressure to the normal point, rapidly cooling and adding malt for the digestion which is to convert the starch into glucose.

The stills in use are continually improved in their minor details, but with no very recent novelty of importance in the principles of their construction.

One of the most interesting modifications of the system of beet-root spirit distillation has been the new method proposed and worked out by Camille Vincent, for utilizing the *vinasse* left behind in the stills. He evaporates this liquor, and submits the residue to destructive distillation in iron vessels (instead of burning off organic matter in the open air). The black porous material found in these vessels is then leached for potash. The condensible portion of the distillate consists of ammoniacal liquor and tar. From the former of these the novel products of tri-methylamine (along with other amine bases) and, from it, methyl chloride are made—this methyl chloride for use in ice machines, in the extraction of perfumes, and in the coal-tar color industry. The tar yields bases of the pyridine series, for which it is not impossible that a use may ere long be found; a single large distillery at Courrières turns out daily, beside other by-products, 100 kilos of methyl alcohol and 1800 kilos of concentrated solution of salts of tri-methylamine.

Vinegar.—Among the results of Pasteur's investigations of organized ferments has been the practice, made use of in France on an industrial scale, of hastening the usual course of acetic fermentation by transplanting or sowing the vinegar *mycoderma*.

In the German, so-called quick method of vinegar making by filtration of the alcoholic fluid through a mass of porous material, usually wood shavings, this mass being traversed at the same time by an ascending current of air, the importance is better recognized now than formerly of carefully regulating not only the temperature but the rate of supply of the liquid to be acidified and the air, since without attention to this notable losses of material may occur, on the one hand by imperfect oxidation and the formation of aldehyde, on the other by more than inevitable evaporation, and by excessive oxidation to carbon dioxide and water.

Artificial Flavoring Essences.—For some years there has been an extensive manufacture of ethers to be used as flavoring materials for confectionary, soda water and other syrups, etc. Those most largely made are the ethyl and amyl formiates, acetates, butyrates and valerianates, but ethyl pelargonate, methyl and ethyl salicylates, and others are also produced.

The most interesting additions of late to the list of such products have been benzoic aldehyde (artificial bitter almond oil), from coal tar toluene, converted by the prolonged action of chlorine into benzylene chloride, to be distilled with an alcoholic solution of an alkaline hydrate; allyl iso-thiocyanate (black mustard oil) from glycerine, distilled with crystallized oxalic acid so as to yield allyl alcohol, and the alkaline thiocyanates so readily obtained as waste products of the treatment of the ammoniacal liquor of gas-works; and artificial vanilline ($C_8H_8O_3$) procured by Tiemann and Haarmann's process from coniferine ($C_{16}H_{22}O_8$), converted into coniferyl alcohol ($C_{10}H_{12}O_3$) with assumption of the elements of water and elimination of glucose, and then oxidized by chromic acid mixture. The high price of the natural vanilla, and its extensive use in connection with chocolate, liqueurs, confectionary, bonbons, etc., gives special importance to the artificial production of its essential constituent.

Artificial Mineral Waters.—These products, occupying a somewhat doubtful position between the ordinary accompaniments of food and therapeutic agents, form the basis of quite an extensive industry, which has grown to its present magnitude within but a few years. With the long used carbonic acid water as a starting point, numerous effervescent waters containing also saline ingredients are made, and omitting the gaseous impregnation, various natural waters, saline, chalybeate, etc., are imitated more or less closely, while of late the artificial modification of the natural contents of certain mineral springs has, with disputed propriety, been added to the directions in which this industry is pushed forward.

J. W. MALLET.

(To be continued.)

NOTES.

On the reversal of the direction of rotation caused by ordinary malic acid by a simple change in the concentration.

It is common to regard the power possessed by many substances of turning the plane of polarization either to the right or the left as something absolute. The substances are either dextro-rotatory or laevo-rotatory. G. H. SCHNEIDER has now shown that, while a concentrated solution of ordinary malic acid is dextro-rotatory, the power diminishes with the addition of water until a solution containing 34.24 per cent. of the acid exerts no influence upon polarized light. If now more water be added the solution is laevo-rotatory, a solution containing only 8.4 per cent. acid turning the plane 2.3° to the left. From a formula given in the paper it is calculated that anhydrous malic acid should turn the plane 5.89° to the right.—(*Ber. d. deutsch. chem. Gesell.* 13, 620.)

The Alkaloids.

A. LADENBURG has previously shown that atropine and hyoscyamine yield the same decomposition-products. He has now succeeded in transforming hyoscyamine into atropine by the three following reactions:

(1) Tropine from atropine and hyoscianic acid from daturine were treated with hydrochloric acid on the water-bath.

(2) Hyoscine from hyoscyamine and tropic acid from atropine were treated in the same way.

(3) Hyoscine from hyoscyamine and hyoscianic acid from hyoscyamine were treated in the same way.

In each case atropine was formed.—(*Ber. d. deutsch. chem. Gesell.* 13, 608.)

On the gases retained by occlusion in aluminium and magnesium.

A short time ago M. DUMAS called attention to the power possessed by molten silver of taking up oxygen in considerable quantity when heated to a high temperature, and of retaining the gas, even after solidification, for a very long period, and perhaps indefinitely. He has since found that if aluminium be heated in a porcelain vessel in a vacuum up to the point of fusion of copper or of silver, it gives up a volume of gas about equal to that of the metal. This was found to be nearly pure hydrogen.

Magnesium treated in a similar way also disengages a gas—about one and a half times its own volume. This was found to be essentially hydrogen, though it was accompanied by the oxides of carbon in greater or less quantity.

During the experiments with magnesium, the author observed that stalactites appeared in the upper part of the vessel in which the metal was heated. On examining the vessel more closely, it was found that all the magnesium had been volatilized and deposited in crystalline form. The crystals were very bright and silver white, and can attain the dimensions necessary for measurements.*—(*Comptes rend.* 90, 1027.)

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* In a later note (*Comptes rend.* 90, 1101) M. Des Cloizeaux describes the crystals of magnesium and gives their measurements. They are rhombohedra.

The Research Fund in England.

During the past session the following sums have been granted from the Research Fund by the Council of the London Chemical Society on the recommendation of the Research Fund Committee:—

30*l*. to Mr. M. Whitley Williams, for the elaboration of an improved method of Organic Analysis.

25*l*. to Mr. M. M. P. Muir, for the study of the Chemical Habitudes and Physical Constants of Bismuth Compounds.

15*l*. to Mr. J. M. Thomson, for experiments on the action of Isomorphous Bodies in exciting the Crystallization of Supersaturated Solutions.

50*l*. to Dr. Wright, for the continuation of his investigations of certain points in Chemical Dynamics.

25*l*. to Mr. F. D. Brown, for the continuation of his investigations of the theory of Fractional Distillation.

30*l*. to Mr. Bolas, for the preparation and investigation of Alloys and Compounds of Chromium.

20*l*. to Dr. Japp, for the investigation of the action of the Organo-zinc Compounds on Quinones.

100*l*. to Dr. Armstrong, for the determination of certain physical properties, especially the Refractive Indices of Typical Chemical Compounds.

100*l*. to Dr. Wright, for the determination of Chemical Affinity in terms of Electrical Magnitudes.

100*l*. to Mr. F. D. Brown, for the determination of the Vapor Tension of Pure Compounds and Mixtures.

In the Report of the Committee occurs this passage: The Committee desire to point out to the Council, and to the Fellows at large, the desirability of obtaining further additions to the fund, for without such contributions as these the incomes arising from investments would have been quite inadequate to meet the legitimate demands upon the fund. It is to be expected, and indeed we hope, that these demands will increase rather than diminish, and it is therefore especially necessary that efforts should be made to increase the income of the fund.*

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* This Research Fund has done much in England to keep alive the spirit of investigation, and no doubt considerable good work has been done in consequence which otherwise would not have been done. This is not the place to discuss the question as to the reason why such good results are reached by such apparently inadequate means. To us it seems perfectly clear. But it may not be out of place to suggest that a Research Fund would find an excellent field in this country.—Ed.

ERRATUM.

In the title of the paper by H. W. Wiley, p. 48, Vol. II, read "chromate" for "sulphate."

VOL. II. [JUNE, 1880.] NO. 3.

AMERICAN CHEMICAL JOURNAL.

CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE COLLEGE.

NO. V.

ON THE DENSITY OF THE VAPORS OF SOME AMMONIUM AND AMMONIA COMPOUNDS.

BY W. G. MIXTER.

Ammonium Acetate.

Cahours* obtained acetamide in trying, by Dumas' method, to find the gas density of ammonium acetate. This salt, as is well known, yields on distillation ammonia, ammonium acetates, and finally acetamide. In the latter the nitrogen is not separated from the carbon by heat. This fact suggested the possibility of the existence of gaseous ammonium acetate at low temperatures and pressures. The results show dissociation analogous to that of ammonium chloride.

The experiments were made with a Hofmann apparatus with a calibrated thermometer hung between the walls of the eudiometer and the jacket tube. The graduations of the barometer and cathetometer used corresponded at common temperatures, and the latter admitted of readings to within ½ mm. The weight of 1 c.c.

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* Liebig's Ann. 128, 75.

of hydrogen was taken at 0.0000896 gram, and that of ammonia gas at 0.000762 gram. The coefficient of expansion used is 0.00366. The ordinary corrections were made for the expansion of mercury and the tension of its vapor. Experiments A were made with 0.060 gram of an ammonium sesquiacetate, which was made by passing ammonia gas into glacial acid and heating the product several hours in an air bath at 100°. Its composition was found by distilling with standard potash into standard acid and titrating both. The result was exactly three molecules of acetic acid to two of ammonia. Whether this composition was accidental was not determined. In the remaining experiments ammonia gas dried by potash was introduced into the eudiometer, and acetic acid was added in very nearly the amount required to form a neutral salt. The ammonia was measured at 100° in B and C, and at 185° in D and E. The acetic acid was purified by crystallization and melted at 15°, except that used in E which melted at 16°. According to Rüdorff,* acetic acid melting at 14.8° contains 0.99 per cent. of water.

	A		B			C		D	E
Weight of Acetic Acid.	..	..	..	0.0323	..	0.0388		0.2437	0.0485
Weight of Ammonia.	..	..	..	0.0096	..	0.0106		0.0691	0.0139
C.c. of Ammonia at 0° and 760 mm.	..	..	..	12.6	..	13.9		90.7	18.2
Temperature.	131.2	183.6	100.4	130.0	182.6	100.4	130.	184.6	185.
Pressure in mm.	274.8	314.4	81.0	101.8	118.5	82.7	120.4	552.6	345.6
Volume in c. c.	111.4	125.0	250.6	257.3	264.4	236.5	250.6	397.1	132.4
Density, H=1.	24.6	21.7	24.0	20.0	18.9	29.3	20.5	20.3	19.4
Pressure on Acetic Acid	148.5	187.1	28.8	47.	58.2	21.6	58.2	261.7	170.4
Density of Acetic Acid in Ammonia Gas.	38.3	30.5	52.3	33.5	29.8	88.4	33.3	33.4	30.6
Naumann's density of Acetic Acid, H=1. †	35.7	30.8	38.5	33.5	..	..	..	32.1	30.8
At pressure.	157.5	191.5	77.7	93.	..	..	..	269.	191.5
And temperature.	130.	185.	100.	130.	..	..	..	185.	185.

The theoretical density of a mixture of four volumes of ammonia and six volumes of acetic acid gas is 21.4, and that of two volumes of each gas is 19.25. It is evident if normal ammonium acetate splits into acetamide and water, or partially into these bodies and partly into ammonia and acetic acid, that the theoretical density of the mixed vapors would be 19.25. No acetamide or water was detected in the crystalline products remaining in the eudiometer

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* Ber. deutsch. chem. Gesell. 3, 390.

† Liebig's Ann. 155, 325.

after each experiment. The crystals were insoluble in ether and gave no odor of acetamide on gently warming. In view of the possibility that acetamide might be formed and then changed back to ammonium acetate, 0.0761 gram of pure acetamide was placed in the eudiometer. It was not all volatilized at 188.5° and a pressure of 266.8 mm. An equivalent of water was then added, and the whole did not evaporate at 185.5° and 523 mm., a pressure not as high as in experiment D. 0.021 gram of acetic acid was then introduced and the eudiometer kept some time at 185°. After cooling the tube was washed with ether. All the crystals dissolved, and the residue remaining after the evaporation had the odor of acetamide. In B, after successive heating to 100°, 130° and 182°, and cooling between each heating, a temperature of 100° was then applied. Before a second observation could be made, which would show whether the heating had been for a sufficient time, the tube broke. The density found was 25 or 1.1 higher than before found. The conclusion is that very little and probably no acetamide was formed in the experiments.

In the table are given Naumann's results on acetic acid, which were obtained under nearly similar conditions of temperature and pressure. His figures are reduced to the hydrogen standard, and correspond within errors of experiment to the densities found for acetic acid when mixed with ammonia gas, except the writer's results at 100°, which are questionable, owing to the uncertainty of complete evaporation. Acetic acid vapor and ammonia gas were slowly passed through thin tubes, a centimeter wide and a meter long, into a small tube holding a delicate thermometer whose bulb was between the two currents of gas. The small tube mentioned was surrounded by a thick jacket tube. The apparatus was heated to 186° by aniline vapor, and no change in temperature was observed, either when the gases met about the thermometer bulb or when the flow of the gases was stopped.

Ammonium Benzoate.

To 4.14 c. c. ammonia gas in the eudiometer was added 0.0285 gram of resublimed commercial benzoic acid, rather more than sufficient to form a normal salt. The observations made at 189° and a pressure of 134.5 mm. reduced to 0° and 760 mm. gave a volume of 8.8 c. c. The density of benzoic acid at 189° and 73.2 mm. in this experiment is 68.2. A direct determination made of the same benzoic acid at the same temperature and a pressure of 119.2 mm. gave 69.3. The theoretical density of the acid is 61.1.

The following determinations were made by Victor Meyer's method. In place of the simple lead bath described by him,* a lead bath was used four inches in diameter holding an inch and a half gas pipe a foot long and closed at its lower end.† In this air-filled gas pipe was placed the evolution tube, and the top of the pipe was closed with two pieces of sheet copper. The lead bath was placed in a small firebrick-lined soldering stove, and was heated by one large Bunsen burner. The thinness of the glass of the evolution tube compelled the use of the air bath in place of a lead bath. A determination of the vapor density of mercury in the apparatus filled with air gave 100.1; theory 99.9.

$2NH_3.SiF_4$.

This compound was prepared by bringing dry silicon fluoride into an excess of dry ammonia. By distilling with potash and titrating 24.22 per cent. of ammonia were found; theory 24.58 per cent. The substance was introduced into the air-filled apparatus in a small platinum tube improvised of foil, which showed no residue after the experiments.

Substance.	c. c. gas at	temperature.	Barometer at 0°.	Density.
0.0331	17.3	23°	759.4	23.8
0.0311	16.5	19°	760.6	23.

A mixture of four volumes of ammonia and two volumes of silicon fluoride has a theoretical gas density of 23. H=1.

$NH_3.BF_3$.

Boron fluoride was evolved from boric oxide, fluor spar and a large excess of oil of vitriol, and was passed into an excess of dry ammonia. The product was pink colored from one black rubber connector used. Ammonia found 20.39 per cent.; theory 19.94 per cent. The apparatus was filled with dry air.

Substance	c. c. gas at	temperature.	Barometer at 0°.	Density.
0.0329	17.6	19.4°	754.8	23.
0.0322	17.4	20.8°	754.4	22.9

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* Ber. deutsch. chem. Gesell. 1878, 2255.

† Since this paper went to press we have received Meier and Crafts' article (this Journal, 2, 108, and Ber. deutsch. chem. Gesell. 1880, 851), in which they describe a similar lead bath.

Another preparation was made with apparatus of only glass, and an excess of boron fluoride was used. The ammonia found was 19.91 per cent. The apparatus was filled with dry air.

Substance.	c. c. gas at	temperature.	Barometer at 0	Density
0.033	17.7	22.6°	765.9	23.
0.0322	17.4	24.6°	765.9	23.1

The theoretical density of a mixture of two volumes of ammonia and two volumes of boron fluoride is 21.3 The temperature of the air bath was higher in the last two experiments, and was above the melting point of zinc. The ammonia boron fluoride melts and evaporates rapidly and leaves no residue when volatilized in platinum, but both the vapor and liquid attack glass slightly. In all the density determinations of the substance the glass showed a faint coating after washing with water, which explains the 1.7 excess found. It is possible that the action on glass was due to ammonium fluoride, but the ammonia estimation of the second preparation does not indicate it, nor was the long wide glass tube corroded through which the boron fluoride passed in the preparation of NH_3BF_3. The substance showed only a trace of silica when treated with water, and a little $2NH_3SiF_4$ would not affect the results. 0.2758 gram gained weight slowly in the air, and showed an increase of 0.008 gram in two days.

$2NH_3.SnCl_4$.

Tin tetrachloride, made by passing chlorine over hot tin, was freed from traces of moisture by distillation from oil of vitriol. It was poured into a dry bottle into which a rapid stream of ammonia was passing. The following is the analysis of the compound:

	Calculated.	Found.	
Sn	40.16	40.14	
Cl_4	48.24	47.78	
$2NH_3$	11.60	11.90	11.85

A portion of the substance exposed to the air a day gained eight per cent. in weight. The apparatus was filled with dry air, and the temperature was considerably above the fusing point of zinc.

Substance.	c. c. gas at	temperature.	Barometer at 0°	Density
0.0598	16.4	23°	750.9	46.
0.0706	19.8	23.4°	750.9	45.

The theoretical density corresponding to six volumes is 48.9.

In the following experiment the apparatus was filled with nitrogen which was freed from traces of oxygen by passing over glowing copper and copper oxide. It was dried by oil of vitriol on broken glass. A residue 0.0014 gram remained in the platinum tube after the experiment, and this was deducted from the weight of substance taken. The heat was the same as before.

Substance volatilized 0.0771, 22.3 c. c. at 29.4°. Bar. at 0° 760. Density, 44.5.

The glass was somewhat acted upon in each experiment with the tin compound, and an iridescence was marked. The substance volatilized too slowly at the melting point of lead and somewhat higher temperatures for a determination by Meyer's method.

Summary.

Ammonium acetates and ammonium benzoate dissociate completely into ammonia and the respective acids when heated under low pressures. $2NH_3.SiF_4$, NH_3BF_3 and $2NH_3.SnCl_4$ dissociate at temperatures above 300° into ammonia and the respective compounds of fluorine and chlorine. This may be easily shown by heating the ammonia compounds in a test tube and testing the reaction of the escaping vapors, which at first are alkaline and afterward acid.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

No. IV.

PARACHLORBENZYL COMPOUNDS.*

By C. Loring Jackson and J. Fleming White.

In the third paper of this series the necessity of a revision of all the so-called parachlorbenzyl compounds was pointed out, and the results were described, which had been obtained from the investi-

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* Proceedings American Academy of Arts and Sciences. Communicated by the Authors.

gation of some of them by Mr. A. W. Field and one of us. This work is now finished, and the present paper contains a description of the preparation and properties of the remaining parachlorbenzyl compounds, which have been heretofore made in an impure state, and also of a few related substances not as yet described.

Parachlorbenzylbromide, melting-point 48½° (made from pure paratoluidine), was used as the starting-point for these compounds, and therefore they cannot contain the isomeric impurities which caused the mistakes of our predecessors.

A comparison, in tabular form, of our more important results with the earlier ones, will be found at the end of the paper.

Parachlorbenzylsulphoacid, $C_6H_4ClCH_2SO_3H$.

This substance was first studied by Böhler,[*] whose paper, published in 1869, contains a description of the preparation of the potassium salt by heating chlorbenzylchloride with neutral potassic sulphite. It was, in fact, one of the papers coming from Strecker's laboratory to illustrate his general method of making sulphoacids,[†] first announced in 1868. The salt was thus obtained in colorless needles which gave with baric chloride glistening crystals of $(C_7H_6ClSO_3)_2Ba.H_2O$; the acid (made from the barium salt with sulphuric acid) formed when heated with an excess of plumbic hydrate, a basic lead salt, $(C_7H_6ClSO_3)_2Pb.PbO_2H_2$, crystallized in scales with a silvery lustre; while with less plumbic hydrate a neutral salt was obtained, which, however, he did not analyze. All these salts were made from ordinary chlorbenzylchloride, and must therefore have been contaminated with the corresponding ortho compounds, as indeed was proved by Vogt and Henninger,[‡] who took up the subject again in 1872, and by fusing the potassium salt (made according to Böhler's method) with potassic hydrate obtained a mixture of salicylic and paraoxybenzoic acids. They did not try, however, to separate the para from the ortho compound, but contented themselves with analyzing Böhler's potassium and barium salts: for the first they found the formula $C_7H_6ClSO_3K.H_2O$; it crystallized from water in concentric groups of large flat needles, from alcohol in pearly plates, lost its water of crystallization at 160°, and was decomposed at higher temperatures: their barium salt agreed in amount of water of crystallization and properties with

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[*] Böhler, Ann. Chem. Pharm. 154, 56.

[†] Strecker, Ann. Chem. Pharm. 148, 90.

[‡] Vogt and Henninger, Ann. Chem. Pharm. 165, 372.

that of Böhler, except that it crystallized in bunches of needles. In preparing their potassium salt Vogt and Henninger observed the formation of an insoluble substance which, purified by crystallization from alcohol, melted at 167° and had the formula $(C_7H_6Cl)_2SO_2$; from the mother-liquors small quantities of two other substances were obtained, melting at 149° and 185°, and apparently having the same composition; they supposed, therefore, that the main product (melting-point 167°) was a mixture of these, and called it chlorinated benzylosulphide,—a name which, according to our present nomenclature, would be altered to dichlorbenzylsulphone. For a revision of their work on this substance, see page 167.

In taking up the subject we followed the method of our predecessors, except that we used sodic instead of potassic sulphite,* which we made by saturating one-half of a strong solution of sodic carbonate with sulphurous dioxide, and then adding to it the other half. After boiling this solution with parachlorbenzylbromide, in the proportion of one molecule of bromide to one of sulphite, in a flask with a return-cooler for seven hours, the smell of the benzylbromide had disappeared; the liquid was therefore allowed to cool, and the insoluble portion removed by filtration. This should have been the sulphone described by Vogt and Henninger, but it melted at about 55° instead of 167°, and a qualitative test showed that it contained no sulphur; from the smell it seemed to be an impure parachlorbenzylalcohol, formed by the action of the water on the bromide, and it was not thought worth while to investigate it farther. Although we have repeated the preparation of the sodium salt many times, we have never observed the formation of Vogt and Henninger's sulphone, but have got invariably this substance with a much lower melting-point.

The *Sodium Salt*, $C_6H_4ClCH_2SO_3Na$, was purified by evaporating the filtrate from the insoluble substance just described to dryness, boiling the residue with absolute alcohol to remove the organic salt from the sodic bromide, and finally recrystallizing from a very little water by spontaneous evaporation.

1.8405 gram of the salt dried *in vacuo* lost when heated to 160° 0.005 gram, corresponding to 0.27 per cent.

0.4160 gram lost at 160° 0.002 gram, corresponding to 0.48 per cent.

As one molecule of water corresponds to 7.30 per cent., it is evi-

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* Potassic sulphite is to be preferred, however.

dent that the salt crystallizes without water, and the slight loss observed is due to a partial decomposition of the substance. This view is confirmed by the fact that the 1.8405 gram used in the first experiment lost only 1 mgr. when the temperature was not allowed to go above 100°.

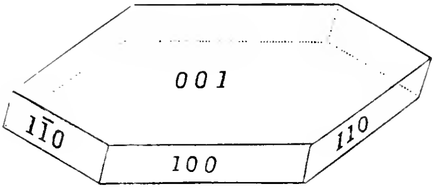
0.5650 gram of the salt dried at 160° gave by the method of Carius 0.3512 gram AgCl and 0.5804 gram $BaSO_4$.

	Calculated for $C_7H_6ClSO_3Na$	Found
Chlorine	15.54	15.37
Sulphur	14.00	14.11

Crystallized from water it forms large flat colorless crystals with pointed ends; from alcohol, pearly scales; it is freely soluble in water, but only sparingly in alcohol.

Dr. F. A. Gooch, who has had the kindness to examine the substance crystallographically for us, reports that "the crystals did not admit of measurement with the goniometer; but an examination of some of the smaller ones, under the microscope, between crossed Nicols, proved them to be triclinic (see figure); the planes of polarization of the Nicols making, in the case of a crystal lying upon its basal plane, angles of about 5° and 175°, or 85° and 95° respectively with the edge 100—001, when the plane of polarization of the ray from the polarizer remains unchanged. The apparent angles of the adjacent edges, when the crystal lies upon its basal plane, are approximately as follows:—

Edge	100—001	upon edge	110—001	141°
"	100—001	" "	$1\bar{1}0$—001	147°
"	110—001	" "	$\bar{1}10$—001	72°



The *Potassium Salt*, $C_6H_4ClCH_2SO_3K$, was made by adding potassic sulphate to the barium salt; the filtrate from the baric sulphate formed was evaporated to dryness, and the organic salt, dissolved out from the excess of potassic sulphate with absolute alcohol, purified by crystallization from water.

1.1328 gram of the salt dried *in vacuo* lost when heated to 160° 0.0075 gram, corresponding to 0.66 per cent.

As one molecule of water corresponds to 6.85 per cent. it is evident that this salt, like that of sodium, is free from water of crystallization.

0.3000 gram of the salt dried at 160° gave by the method of Carius 0.1760 gram AgCl.

0.3165 gram gave by the same method 0.3025 gram $BaSO_4$.

0.3065 gram gave, when heated with pure H_2SO_4, 0.1075 gram of K_2SO_4.

	Calculated for $C_7H_6ClSO_3K$.	Found.
Chlorine	14.50	14.50
Sulphur	13.08	13.13
Potassium	15.98	15.75

It resembles the sodium salt closely in appearance, but is much more soluble in alcohol. As, therefore, the separation of this salt from potassic bromide would be easier than that of the corresponding sodium compounds, it is better in making a salt of the sulphoacid from parachlorbenzylbromide to use potassic in place of sodic sulphite.

To prepare the other salts of the parachlorbenzylsulphoacid the mother-liquor of the sodium salt was treated with a small quantity of a solution of plumbic acetate, which precipitated plumbic bromide and sulphite; after these had been removed by filtration an excess of plumbic acetate threw down the lead salt of the sulphoacid, which was purified by recrystallization from water, and then decomposed with sulphuretted hydrogen; the filtrate from the plumbic sulphide was concentrated by evaporation, and the solution of parachlorbenzylsulphoacid thus obtained used in the preparation of the following salts.

The *Barium Salt*, $(C_6H_4ClCH_2SO_3)_2Ba.2H_2O$, was made by boiling the acid with pure baric carbonate. It can also be prepared by the addition of baric chloride to the sodium salt, but in this case it was found hard to free it from the excess of baric chloride.

0.9290 gram of the salt dried *in vacuo* lost when heated to 160° 0.0565 gram.

0.5408 gram lost 0.0332 gram.

	Calculated for $(C_7H_6ClSO_3)_2Ba.2H_2O$.	Found.	
Water	6.16	6.08	6.12

0.1575 gram of the salt dried at 160° gave, after precipitation with dilute H_2SO_4, 0.0680 gram of $BaSO_4$.

0.4620 gram gave 0.1995 gram $BaSO_4$.

	Calculated for $(C_7H_6ClSO_3)_2Ba$.	Found.	
Barium	25.00	25.38	25.39

It crystallizes from water in radiated bunches of white needles which are moderately soluble in water.

The *Calcium Salt*, $(C_6H_4ClCH_2SO_3)_2Ca.7H_2O$, was made by warming the aqueous solution of the acid with calcic carbonate, filtering and allowing the concentrated filtrate to evaporate spontaneously; it was purified by recrystallization from water.

0.5805 gram of the air-dried salt lost *in vacuo* 0.1033 gram; when heated to 160°, 0.0332 gram; making in all 0.1365 gram.

0.9536 gram lost *in vacuo* 0.1506 gram; when heated to 160°, 0.0552 gram; making in all 0.2058 gram.

	Calculated for $(C_7H_6ClSO_3)_2Ca.7H_2O$.	Found.	
Water	21.84	23.51	21.58

	Calculated for $(C_7H_6ClSO_3)_2Ca.2H_2O$.	Found.	
Water	7.39	6.96	6.87

The air-dried salt, therefore, contains seven molecules of water of crystallization, five of which it gives up *in vacuo*, while a heat of 160° is necessary to remove the whole of its water. The very high result of the first water determination was undoubtedly due to hygroscopic moisture in the air-dried salt.

0.6976 gram of the salt dried at 160° gave, after precipitation with ammonic oxalate and ignition over the blast-lamp, 0.085 gram of CaO.

	Calculated for $(C_7H_6ClSO_3)_2Ca$.	Found.
Calcium	8.87	8.70

It forms rhombic crystals so nearly square that they look like flattened cubes, freely soluble in water.

The *Copper Salt*, $(C_6H_4ClCH_2SO_3)_2Cu.2H_2O$, was made by warming the aqueous solution of the acid with pure cupric carbonate, and concentrating the filtrate on the water-bath; the crystals thus obtained were recrystallized from water.

0.7400 gram of the salt dried *in vacuo* lost when heated to 160° 0.0525 gram.

	Calculated for $(C_7H_6ClSO_3)_2Cu.2H_2O$.	Found.
Water	7.08	7.05

0.5000 gram of the salt dried at 160° gave by precipitation with sodic hydrate 0.0833 gram of CuO.

	Calculated for $(C_7H_6ClSO_3)_2Cu$.	Found.
Copper	13.37	13.30

It crystallizes in pale green needles grouped in bundles, and is readily soluble in water.

The neutral *Lead Salt*, $(C_6H_4ClCH_2SO_3)_2Pb.H_2O$, was made by treating an aqueous solution of the acid with plumbic hydrate not in excess, the solution was evaporated *in vacuo*, and the crystals washed with a little water to free them from the acid. It is probable from the resemblance in crystalline form, that the precipitate formed on adding a strong solution of the sodium salt to plumbic acetate consists of this salt.

0.8695 gram of the salt dried *in vacuo* lost when heated to 100° 0.0261 gram.

0.1910 gram lost at 100° 0.0056 gram.

0.1900 gram of the salt dried *in vacuo* gave, after precipitation with dilute H_2SO_4, 0.0902 gram of $PbSO_4$.

	Calculated for $(C_7H_6ClSO_3)_2Pb.H_2O$.	Found.	
Water	2.83	3.00	2.93
Lead	32.55	32.43	

0.1742 gram of the salt dried at 100° gave 0.0850 gram of $Pb.SO_4$.

	Calculated for $(C_7H_6ClSO_3)_2Pb$.	Found.
Lead	33.50	33.34

It crystallizes in long white needles grouped in sheaves or stars, which are not freely soluble in water.

Two *Basic Lead Salts* were obtained by treating the mother-liquor from the preceding salt with an excess of plumbic hydrate; one crystallized from water by spontaneous evaporation in little spheres made up of radiating needles, and seemed to be free from water of crystallization, although it blackened and lost weight at 160°.

0.3384 gram of the salt dried at 100° gave, after precipitation with dilute H_2SO_4, 0.2890 gram of $Pb.SO_4$.

	Calculated for $(C_7H_6ClSO_3)_2Pb_3O_2$.	Found
Lead	58.35	58.34

The formula of this salt is therefore $(C_6H_4ClCH_2SO_3)_2Pb_3O_2$. The second salt, which crystallized from a hot concentrated solution in white scales, had the formula $C_6H_4ClCH_2SO_3PbOH.H_2O$.

0.2128 gram of the salt dried *in vacuo* lost at 120° 0.0087 gram.

0.2747 gram of the salt dried *in vacuo* gave with dilute H_2SO_4 0.1870 gram $PbSO_4$.

	Calculated for $C_7H_6ClSO_3PbOH.H_2O$.	Found.
Water	4.02	4.08
Lead	46.26	46.49

To obtain the *Free Acid* the lead salt, which had been purified with great care, was suspended in water, and decomposed with sulphuretted hydrogen, the filtrate from the plumbic sulphide formed was evaporated in a stream of sulphuretted hydrogen, first on the water bath, and finally at a still lower temperature, until it had attained the consistency of syrup; it was then put *in vacuo*, where, after standing some time, it crystallized in square plates, which, however, soon turned yellow, while fumes were given off which smelt of hydrochloric acid and benzaldehyd. These yellow crystals melted at 108°, but the evidences of decomposition were so marked that we do not consider this the true melting-point of the acid, nor did it seem worth while at present to follow the investigation of such an unstable substance farther.

The *Chloride*, $C_6H_4ClCH_2SO_2Cl$, was made by grinding the dry sodium salt, with phosphoric pentachloride, and afterward warming the mixture gently in a porcelain dish on the sand bath: the oily mass thus obtained gave with water the chloride as a heavy oil, which soon solidified, and was purified by crystallization from ether.

0.1410 gram of substance gave by the method of Carius 0.1768 gram of AgCl and 0.1470 gram of $BaSO_4$.

	Calculated for $C_7H_6ClSO_2Cl$.	Found.
Chlorine	31.55	31.02
Sulphur	14.22	14.32

It forms white flattened crystals, often arranged in indistinct pennate groups, and having an aromatic odor; melting-point 85½°; it is insoluble in water, soluble in ether and alcohol, but seems to be decomposed by the latter.

Parachlorbenzylsulphide, $(C_6H_4ClCH_2)_2S$.

Pauly* described this substance, which he obtained from chlorbenzylchloride (or bromide), by the action of an alcoholic solution of potassic sulphide, as a thick brown oil, with an unpleasant odor; and adds, that it did not solidify even after standing several days.

On warming an alcoholic solution of parachlorbenzylbromide with sodic sulphide (prepared by saturating one-half of an alcoholic solution of NaOH with H_2S, and then adding the other half) we obtained by precipitation of the product with water a heavy oil, which we dissolved in hot alcohol; on cooling this saturated solution a purer oil separated, that solidified on standing over night, and was then purified by recrystallization from hot alcohol.

0.2760 gram of the substance dried *in vacuo* gave on combustion 0.5970 gram of CO_2 and 0.1110 gram of H_2O.

	Calculated for $(C_7H_6Cl)_2S$.	Found.
Carbon	59.35	59.00
Hydrogen	4.24	4.47

It forms thick white needles, often seven centimetres long, with very little odor; from a hot alcoholic solution, it is sometimes deposited as an oil, which solidifies by scratching with a sharp glass rod; melting point, 42°; it cannot be sublimed without decomposition; essentially insoluble in water, soluble in cold, more freely in hot alcohol, easily soluble in ether, benzol, carbonic disulphide, and glacial acetic acid.

Diparachlorbenzylsulphone $(C_6H_4ClCH_2)_2SO_2$, was made by adding the calculated amount of chromic anhydride in small quantities at a time to the preceding substance, both bodies being dissolved in glacial acetic acid; the product of the oxidation, washed with water until free from compounds of chromium, was purified by crystallization from alcohol. The substance was also formed by the oxidizing action of the air on parachlorbenzylsulphide.

0.3510 gram of the substance gave, according to Carius, 0.3195 gram of AgCl and 0.2610 gram of $BaSO_4$.

	Calculated for $(C_7H_6Cl)_2SO_2$.	Found.
Chlorine	22.54	22.51
Sulphur	10.16	10.21

It crystallizes in very small needles, melts at 165°, and cannot be sublimed without decomposition; it is essentially insoluble in

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* Pauly, Ann. Chem. Pharm. 167, 187.

water, readily soluble in alcohol, ether, carbonic disulphide, glacial acetic acid, and ligroine. The melting-point of this substance (165°) is essentially the same as that of the sulphone (167°), obtained in largest quantity by Vogt and Henninger from the action of chlorbenzylchloride on potassic sulphite, and mentioned on page 160. The isomere, melting at 149°, obtained by them, was probably the corresponding orthochlorbenzylsulphone, but it is hard to understand what the substance melting at 185° could have been. It will be remembered that we did not succeed in obtaining a sulphone when we repeated their work.

Parachlorbenzylmercaptan, $C_6H_4ClCH_2SH$.

The first attempt to prepare this substance was made in 1860 by Beilstein,* who heated a somewhat indefinite mixture of dichlor-substitution products of toluol with potassic sulphydrate, and obtained an oil which on exposure to the air yielded well-formed octahedra with a vitreous lustre, melting from the first preparation at 77°–78°, from the second at 84°–85°. Later, Neuhof† tried the same experiment with a mixture of ortho- and parachlorbenzyl-chloride, and confirmed the results of Beilstein, as the melting point of his crystals was 84°–85°. In repeating their work, we found that on mixing alcoholic solutions of parachlorbenzylbromide and KSH (prepared by saturating an alcoholic solution of potassic hydrate with sulphuretted hydrogen), heat was given off, and the action was finished without the aid of external heat in about half an hour; on adding water to the product, a dark-colored oil was precipitated, which, purified by distillation with steam, was frozen by immersion in ice and salt, and recrystallized from alcohol with the aid of a freezing mixture.

0.2560 gram of the substance dried *in vacuo*, treated by the method of Carius, gave 0.2276 gram of AgCl and 0.3750 gram of $BaSO_4$.

	Calculated for C_7H_6ClSH.	Found.
Chlorine	22.40	22.00
Sulphur	20.19	20.12

At ordinary temperatures, it is a colorless liquid with a most repulsive and nauseating smell; in a freezing mixture of ice and salt, it solidifies in white crystals, which melt from 19° to 20°. We are not certain that this is the true melting-point of the substance, as a

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* Beilstein, Ann. Chem. Pharm. 116, 336.

† Neuhof, Ann. Chem. Pharm 147, 339.

small portion of it may have been converted into the disulphide by the action of the air, and the elementary analysis cannot show the presence of this impurity, but the number here given cannot be very far from the truth, as we got in no case a melting-point much above 20°, and the substance was reduced with zinc and dilute sulphuric acid, so as to convert any disulphide into mercaptan, before taking some of the melting-points. It distils with steam, and mixes readily with alcohol, ether, benzol, and carbonic disulphide, but not with water. Yellow mercuric oxide attacks it with great energy, and converts it into the following compound:

Parachlorbenzylmercaptid $(C_6H_4ClCH_2S)_2Hg$, was purified by repeated crystallization from boiling alcohol.

0.4820 gram of the substance dried *in vacuo* gave by precipitation with H_2S 0.2175 gram of HgS.

	Calculated for $(C_7H_6ClS)_2Hg$.	Found.
Mercury	38.84	38.91

It forms light white needles without odor, which seem to have no definite melting-point, although the substance turns red or black, and shrinks to about one-half of its original volume in the neighborhood of 160°; it is insoluble in water, very slightly soluble in ether, benzol, carbonic disulphide, glacial acetic acid, and cold alcohol; more readily, but still not very freely, soluble in hot alcohol. It is decomposed by sulphuretted hydrogen into mercuric sulphide and the mercaptan.

Parachlorbenzyldisulphide, $(C_6H_4ClCH_2)_2S_2$.

This substance was made in several different ways:—(1) When parachlorbenzylbromide was boiled for two or more days with an alcoholic solution of potassic sulphydrate, on evaporating off the alcohol a mixture of the oily mercaptan with needles of the disulphide was obtained, which was exposed to the air for some time to oxidize the mercaptan. (2) The parachlorbenzylmercaptan was treated with the calculated amount of bromine dissolved in ether; the reaction is as follows:

$$2C_7H_6ClSH + Br_2 = (C_7H_6Cl)_2S_2 + 2HBr.$$

When a large excess of bromine was added, the product was an oil with an aromatic smell, the study of which is postponed for the present. (3) Parachlorbenzylbromide was warmed with an alcoholic solution of sodic disulphide (Na_2S_2) obtained by dissolving the calculated amount of flowers of sulphur in an alcoholic solution of sodic sulphide (Na_2S). The products of all these methods had the same melting-point and properties.

For analysis, a specimen prepared according to the first method was purified by crystallization from alcohol and dried *in vacuo*.

0.3925 gram of the substance gave on combustion 0.7615 gram of CO_2 and 0.1475 gram of H_2O.

0.2540 gram gave, according to the method of Carius, 0.3780 gram of $BaSO_4$.

	Calculated for $(C_7H_6Cl)_2S_2$.	Found.
Carbon	53.34	52.91
Hydrogen	3.81	4.17
Sulphur	20.32	20.44

It forms flattened white needles with a disagreeable smell, somewhat like that of the mercaptan, but much less nauseating: melting-point 59°; insoluble in water, readily soluble in alcohol, glacial acetic acid, and ligroine, very soluble in ether, benzol, and carbonic disulphide. Neither mercuric oxide nor mercuric chloride has any action upon it. Nascent hydrogen made from zinc and dilute sulphuric acid converts it into the mercaptan.

Beilstein, and afterward Neuhof, obtained their so-called mercaptan (melting-point 84°–85°) by boiling the substances together for a long time, which we find, as already stated, gives the disulphide as principal product; furthermore, their crystals were formed only after long exposure of the liquid product of the reaction to the air. It would seem, therefore, that their substance must have been the disulphide, the percentage composition of which is essentially the same as that of the mercaptan, and therefore the two substances could not be distinguished by analysis, but only by treatment with mercuric oxide, which they do not seem to have tried. On the other hand, the melting-point of their substance (84°) is much higher than that of ours (59°), and it is certainly strange that a mixture of an ortho- and para-compound should melt at a higher temperature than the pure para-compound; they also describe it as crystallizing in vitreous octahedra, while our substance crystallizes even by slow evaporation of a benzole solution in the flattened needles already mentioned.

Parachlorbenzyldisulphidedioxide, $(C_6H_4ClCH_2)_2S_2O_2$, was made by adding the necessary amount of chromic anhydride dissolved in glacial acetic acid to a weighed quantity of the disulphide also dissolved in glacial acetic acid; on the addition of water, an oil was deposited, which became solid on standing in the cold, and was purified by crystallization from alcohol.

0 5870 gram of the substance dried *in vacuo* gave, by combustion, 1.0390 gram CO_2 and 0.1838 gram of H_2O.

	Calculated for $(C_7H_6Cl)_2S_2O_2$.	Found.
Carbon	48.42	48.27
Hydrogen	3.45	3.48

It is a waxy solid, which becomes crystalline after some time: the melting-point of the specimen analyzed was 120°; it is insoluble in water, readily soluble in alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid.

The *Parachlorbenzylethylether* was made by boiling parachlorbenzylbromide with an alcoholic solution of sodic hydrate: the product was precipitated with water, and the oil purified by distillation with steam. It was a colorless liquid, which distilled over between 215°-225°, and did not solidify when cooled to —12°. As its properties therefore agreed essentially with those ascribed to it by Naquet,[*] who made it as we did, and Neuhof,[†] who obtained it from the chlorbenzylacetate and alcoholic potassic hydrate, we did not think it worth while to analyze or study it more carefully.

We have thus brought our revision of the parachlorbenzyl compounds to an end; the only one previously obtained that we have not studied is the amide of the parachloralphatoluylic acid, which we did not succeed in obtaining by the action of potassic cyanide on parachlorbenzylbromide, although Neuhof made it in this way from the chlorbenzylchloride. It is possible, but not very probable, that this difference between his results and ours is due to the fact that he used the chloride while we used the bromide.

For convenience of comparison, the melting-points of the substances described in this paper, with those given by our predecessors, are collected in the following table, to which is added a comparison between the amounts of water of crystallization in the salts of the parachlorbenzylsulphoacid, in those heretofore described as such, and in the corresponding salts of the benzylsulphoacid.[‡]

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[*] Naquet, Ann. Chem. Pharm., Supp. 2, 249.

[†] Neuhof, Ann. Chem. Pharm. 147, 339.

[‡] Bohler, Zeitschrift der Chemie, 1868, 440.

Comparison of Melting-points.

Formula of Substance.	Correct Melting-point.	Former Melting-point.	Authority for former Melting-point.
$C_6H_4ClCH_2SO_2Cl$	85½°		
$(C_6H_4ClCH_2)_2S$	42°	Oil	Pauly.
$(C_6H_4ClCH_2)_2SO_2$	165°	167°	Vogt and Henninger.
$C_6H_4ClCH_2SH$	19°	77°–78° 84°–85 84°–85°	Beilstein. .... Neuhof.
$(C_6H_4ClCH_2)_2S_2$	59	See above.	
$(C_6H_4ClCH_2)_2S_2O_2$	120°		
$C_6H_4ClCH_2OC_2H_5$	Oil	Oil Oil	Naquet. Neuhof.

Comparison of the Composition of certain Salts of Chlorbenzyl and Benzyl Sulphoacids.

Name of Salt.	Chlorbenzylsulphoacid.			Benzyl Sulphoacid.
	Para.	Bohler.	Vogt and Henninger.	
Sodium	No H_2O	....	....	....
Potassium	No H_2O	H_2O	H_2O	H_2O
Barium	$2H_2O$	H_2O	H_2O	$2H_2O$
Calcium	$7H_2O$ or $2H_2O$	....	....	$2H_2O$
Copper	$2H_2O$	....	....	No good crystals.
Lead	H_2O	....	....	No H_2O
Basic Lead	$PbO_2H_2.2H_2O$	PbO_2H_2	....	PbO_2H_2
Basic Lead	$2PbO$	....	....	....

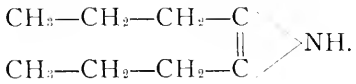
PRELIMINARY NOTE ON THE SYNTHESIS OF METHYLCONINE AND CONSTITUTION OF CONINE.

By Arthur Michael and Charles Gundelach.

The action of alcoholic ammonia on normal butylaldehyde was examined in 1871–2 by H. Schiff, who obtained, on allowing a mixture of these compounds to stand for six months and heating subsequently the bases thus formed to a high temperature, among other products a tertiary base, isomeric with conine, and which he called paraconine. We have obtained this base more easily by heating normal butylidene chloride (CH_3-CH_2-CH_2-$CHCl_2$) with alcoholic ammonia for six hours at 180°, and have characterized the base obtained as paraconine, by an analysis of the platinum salt, its behavior toward chlorhydric acid, and by the formation of a liquid addition-product with ethyl iodide.

Of greater interest is the result obtained in the action of an alcoholic solution of methylamine on normal butylidene chloride, under the same conditions as above. The base thus formed appears to be identical with natural methylconine. This we infer from its physical properties and analysis, behavior toward chlorhydric acid, and especially from the formation of a solid addition-product by heating it on a water-bath with ethyl iodide and alcohol, which is apparently identical with the ammonium iodide compound obtained by von Planta and Kekulè in the same manner from natural methylconine.

These and other experiments, which we have made in the hope of ascertaining the constitution of conine, have led us to accept the following rational formula as the most probable for conine:



Methylconine being a tertiary base, the amine hydrogen is replaced in the formula by a methyl group. Should a more thorough investigation of the base show that it is identical with methylconine, this would be the first instance of a synthesis of a natural alkaloid, since the product found in nature consists of a mixture of conine and methylconine. Possibly, by distilling the chloride of methylconine in a current of chlorhydric acid, the synthesis of conine may be effected.

This research will, owing to the difficulty of obtaining the crude products and the small yield obtained of the base, proceed slowly; and we hope by this note to reserve the study of the reaction in question.

LABORATORY NOTES FROM THE UNIVERSITY OF CINCINNATI.

XIII.—ON A NEW VARIETY OF TETRAHEDRITE.

By F. W. Clarke and Mary E. Owens.

Some months ago there was submitted to one of us for investigation a mineral from an unknown locality in Arizona. It was massive, steel-gray in color, and bore all the ordinary characteristics of tetrahedrite. Its specific gravity, however, was a trifle lower than is usual for the species, ranging from 4.34 to 4.36. Mixed with it were trifling quantities of galena, copper pyrites and a quartzose gangue. An analysis of the mineral, carefully freed from impurities, led to the following results :

	I.	II.	III.	IV.	Mean.
S	21.67	......	......	......	21.67
Sb	......	24.57	24.86	......	24.72
Cu	......	33.68	......	33.38	33.53
Pb	......	15.73	16.72	......	16.23
Ag	1.78	......	......	1.82	1.80
Fe	......	......	......	.56	.56
					98.51

A trace of arsenic was not estimated; nor was any account taken of a fraction of one per cent. of gangue from which the mineral could not be perfectly separated. Another analysis was begun by Mr. H. B. Wilson, but not finished. His figures were unfortunately lost, and we can only say concerning them that his estimate for sulphur closely confirmed the value given above.

It will at once be seen that this mineral agrees in composition with no species hitherto described. Its density, however, and its atomic ratios, clearly identify it as tetrahedrite in which a portion of the copper has been replaced by lead. The high percentage of the latter metal might be attributed to an admixture of galena were it not for the low specific gravity. It might perhaps be regarded as an independent species, in which case its claims to recognition would be precisely analogous to those of the other derived tetrahedrites, freibergite and spaniolite.

XIV.—SPECIFIC GRAVITY DETERMINATIONS.

BY F. W. CLARKE.

The following determinations of specific gravity have been made by students under my immediate supervision. The salts were weighed in benzol, and the density of water at 4° has been taken as unity. To each figure, which is the mean of several closely concordant estimations, I append the name of the determiner.

Ammonium perchlorate,	NH_4ClO_4	1.885 at	25°	A. Stephan.
Barium dithionate,	$BaS_2O_6.4H_2O$	3.055	24.5°	"
Magnesium iodate,	$MgI_2O_6.4H_2O$	3.283	13.5°	E. P. Bishop.
Barium bromide,	$BaBr_2.2H_2O$	3.680	24.3°	A. Harper.
Barium cadmium bromide,	$BaCdBr_4.4H_2O$	3.665	24°	"
Barium iodide,	$BaI_2.7H_2O$	3.673	20.3	H. W. Leonard.
Cadmium potassium iodide,	$K_2CdI_4.2H_2O$	3.359	21°	"
Cobalt hypophosphite,	$CoP_2H_4O_4.6H_2O$	1.809	18.5°	G. C. Nye.
Nickel "	$NiP_2H_4O_4.6H_2O$	1.841	19.3	"
Zinc "	$ZnP_2H_4O_4.6H_2O$	2.017	19.6°	"
Ammonium sulphate,	$(NH_4)_2.SO_4$	1.765	20.5°	H. B. Wilson.
Trimercuric chromate,	$3HgO.CrO_3$	7.1711	18.6°	Helena Stallo.
Manganese oxalate,	MnC_2O_4	2.444	21.4	L. R. Freeman.
Cobalt "	CoC_2O_4	2.310	19.8°	"
Nickel "	NiC_2O_4	2.227	19°	"
Cadmium "	CdC_2O_4	3.315	17.5°	"
Zinc "	ZnC_2O_4	2.564	20.1	H. B. Wilson.
Stannous "	SnC_2O_4	3.573	21.3	"
Oxalic acid,	$H_2C_2O_4.2H_2O$	1.653	18.5°	"
Roseocobalt iodosulphate,	$Co_2(NH_3)_{10}(SO_4)_2I_2$	2.144	20.5	"
Cadmium formate,	$CdC_2H_2O_2.2H_2O$	2.429	20	H. Breen.
Zinc "	$ZnC_2H_2O_2.2H_2O$	2.157	21.3°	"
Cadmium barium formate,	$(BaCd)C_2H_2O_2$	2.733	19.7°	"
Barium formate,	$BaC_2H_2O_2$	3.471	23°	D. Stern.
" propionate,	$BaC_6H_{10}O_2$	2.067	22.3°	"
" butyrate,	$BaC_8H_{14}O_2$	1.768	22°	"
Diammonic citrate,	$(NH_4)_2C_6H_6O_7$	1.479	22	R. S. Blakemor
Trisodic "	$2(C_6H_5Na_3O_7).11H_2O$	1.858	23.8°	"
Barium tartar emetic,	$BaC_8H_8SbO_{14}.2H_2O$	3.112	19°	O. T. Joslin.
Barium tartrate,	$BaC_4H_4O_6$	2.973	21.4	"
Lead "	$PbC_4H_4O_6$	4.012	17.2°	"
Strontium "	$SrC_4H_4O_6$	2.582	17.3	"
" "	$SrC_4H_4O_6.4H_2O$	1.966	19.8°	"
Cobalt thiosulphate,	$CoS_2O_3.6H_2O$	1.935	25°	D. S. Oliver.
Magnesium "	$MgS_2O_3.6H_2O$	1.818	24	"
Ammonium copper chloride,	$2NH_4Cl.CuCl_2.2H_2O$	1.984	24°	C. S. Evans.
" " sulphate,	$2(NH_4)_2SO_4.CuSO_4.6H_2O$	1.871	22°	"
Copper ammonio-sulphate,	$CuSO_4.4NH_3.H_2O$	2.133	24.3	"
" ammonio-nitrate,	$CuN_2O_6.4NH_3$	1.905	21.5°	"

The subjoined determinations were made by myself:

Thorium sulphate,	$Th(SO_4)_2$	4.053 at	22.8
" "	$2Th(SO_4)_2.9H_2O$	3.398	24
" oxalate,	ThC_4O_8	4.637	16
Strychnine,		1.359	18
Strychnine chloroplatinate,		1.779	13.5°
Berberine hydrochlorate,		1.397	19.4
" chloroplatinate,		1.758	19
Ethylamine "		2.252	19.1

CONCERNING IODINE.

By Victor Meyer.*

While reserving the right to consider in detail the criticism of my experiments on iodine which Messrs. Crafts and Meier have given in their extremely interesting paper on "The Vapor Density of Iodine," I take this opportunity to communicate briefly the following observation: By a modification of the method of heating I have succeeded in reaching a materially higher temperature than that which has thus far been employed by me in estimating vapor densities. At the temperature now attainable for heating the vessels, iodine has no longer the density corresponding to $\frac{2}{3}I_2$, but it agrees very closely with the value calculated for I. That the method of heating and of the experiment in general are capable of giving accurate results was first established by making an estimation of the vapor density of mercury under exactly the same conditions as those which existed in the experiments described below. This gave:

$S = 0.0861$; $t = 15.3°$; $B = 716.9$ mm.; $V = 10.8$.

Found.	Calculated for Hg.
7.03	6.91

The estimations made with iodine gave the following results:

I. $S = 0.0642$; $t = 16°$; $B = 718.2$ mm.; $V = 12.5$.
II. $S = 0.0639$; $t = 15°$; $B = 717.0$ mm.; $V = 12.35$.
III. $S = 0.0600$; $t = 21°$; $B = 722.5$ mm.; $V = 11.8$.

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* Communicated to this Journal.

Found.		
I.	II.	III.
4.53	4.55	4.57

The calculated values are for $\begin{cases} I_2 = 8.79 \\ \frac{2}{3}I_2 = 5.83 \\ I = 4.39. \end{cases}$

The question whether, in accordance with the view of Mr. Crafts, the minimum density is reached in the value for I (4.39), or whether, as is assumed in the chlorogen-hypothesis* suggested by me, the limit of dissociation is given in the value $\frac{1}{3}I_2$ (2.93), may be tested by vapor density determinations made at still higher temperatures than that already reached. I hope to reach the temperatures necessary for these experiments by the use of the oil blast-furnace recently described by Deville and Troost, in which porcelain may be melted; and I hope to be able to use graphite for the vessels in case it should be found impossible to use porcelain.

I can not close this communication without expressly stating that the credit of having first distinctly exceeded the dissociation maximum of $\frac{2}{3}I_2$, previously reached by me, undoubtedly belongs to Mr. Crafts.

ZURICH, *May*, 1880.

ON THE DETERMINATION OF BARIUM AS CHROMATE.

By H. N. MORSE.

As a means of estimating barium in the presence of strontium, calcium and magnesium, F. Frerichs† recommends precipitation from solutions containing acetic acid by means of chromate of potassium, collection of the precipitate upon a weighed filter, and washing with dilute acetic acid until a colorless filtrate is obtained. The method having yielded, in the hands of our students, very unsatisfactory results, it was decided to subject it to a careful examination. The work is still incomplete; but in view of the fact that it has been necessarily suspended for a few months, it is thought best to briefly record the results thus far obtained.

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* Chem. Centralblatt, 1879, 577.

† Ber. d. d. ch. Gesell. 1874, 800, 956.

Solutions of the pure chlorides of barium, strontium and calcium were prepared, and the strength of each carefully determined. The acetic acid used was proved to be free from hydrochloric and sulphuric acids, and its strength was ascertained by means of a standard solution of caustic potassa. The chromate of potassium employed was purchased as chemically pure, and assumed to be so after three recrystallizations. The filters were of the best Swedish paper, and had been soaked in very dilute hydrochloric acid. They were in all cases dried three hours at a temperature between 110° and 115°, and as nearly as possible at 112°. When the variation in weight after two successive heatings amounted to less than half a milligram the mean was assumed to be correct. If the variation amounted to more than half a milligram the heating was repeated until three weights whose greatest divergence was less than a milligram were obtained. The mean of the three was then taken. The weighing glasses used were found to vary in weight from day to day according to the humidity of the atmosphere. The maximum variation observed was about one milligram. The weighings obtained are therefore believed not to be reliable to within less than one milligram, since no analysis could be completed in a single day. It was discovered too late to repeat the work that the results are vitiated to some extent by the presence of a minute quantity of sulphate in the chromate of potassium, and by the fact that the filters used lose weight when washed with acetic acid of any considerable strength. The vitiation from these causes is not, however, sufficient to destroy their value as preliminary results.

Frerichs states that the presence of acetic acid is a necessary condition to the complete precipitation of the barium as chromate, and the two following experiments tend to prove the correctness of this observation. 10 c. c. of the standard solution of barium chloride were in each case diluted with water, treated with double the quantity of potassium chromate required by the barium and allowed to stand about forty-eight hours. The precipitates were then collected upon weighed filters and thoroughly washed with water. The weights found were 0.2313 gram and 0.2322 gram, while the calculated weight was only 0.2291 gram. The excess in the first case is 0.0022 and in the second 0.0031 gram. Nevertheless both filtrates became quite cloudy on being treated with dilute sulphuric acid, showing that the barium had not been completely precipitated.

The next step was to ascertain whether the precipitation of the barium is complete in the presence of acetic acid. To this end several portions of ten or twenty c. c. of the standard solution of barium chloride were measured off, diluted with water, and treated with about five c. c. of thirty per cent. acetic acid and double the quantity of chromate of potassium required by the barium. After about forty-eight hours the precipitates were collected upon weighed filters and thoroughly washed with water. The following results were obtained :

$BaCl_2$ taken.	$BaCrO_4$ calc.	$BaCrO_4$ found.	Difference.
I. 10 c. c.	0.2291 gr.	0.2289 gr.	0.0002 gr.
II. "	"	0.2278	0.0013
III. 20 c. c.	0.4582 gr.	0.4570	0.0012
IV. "	"	0.4575	0.0007

The solubility of the chromate of barium in acetic acid was then examined into. In all of these experiments the precipitate was washed with the prepared liquid until the volume of the filtrate reached 250 c. c. The filtrate was then allowed to pass again through the filter. The portions of chromate of barium first experimented upon were those marked I. and II. in the above table. The wash liquid used was a one per cent. acetic acid.

Precipitate I. lost by the first washing 0.0248 gram, or 10.87 per cent.; by the second 0.0229 gram, or 11.22 per cent.

Precipitate II. lost by the first washing 0.0244 gram, or 10.71 per cent.; by the second 0.0282 gram, or 13.81 per cent.

The filtrates were clear, but decidedly yellow in color, and gave precipitates of sulphate of barium on being treated with dilute sulphuric acid.

It appears from these results that, though barium can be completely precipitated in the presence of acetic acid by chromate of potassium, the precipitate cannot be washed with even the dilutest solutions of acetic acid without loss. The only possible explanation of this apparent contradiction is that the chromate of barium is in the first case prevented from going into solution by the presence of an excess of chromate of potassium ; and, if so, it should not dissolve when washed with acetic acid containing chromate of potassium. In order to test the correctness of this explanation, known weights of chromate of barium were washed with solutions of acetic acid of various concentrations, and containing different quantities of chromate of potassium. As before, the precipitates were washed until the volume of the filtrate reached 250 c. c., after which the filtrate was allowed to pass again through the filter. The following results were obtained:

Experiment A.

Weight of chromate of barium, 0.2278 gram.

Wash liquid, 1 per cent. acetic acid containing about six molecules of chromate of potassium to each one hundred molecules of the acid.

Loss in weight, 0.0001 gram.

Experiment B.

Weight of chromate of barium, 0.45695 gram.

Wash liquid, 2 per cent. acetic acid containing about three molecules of chromate of potassium to each one hundred molecules of the acid.

Loss in weight, 0.0008 gram.

Experiment C.

Weight of chromate of barium, 0.4561 gram.

Wash liquid, 10 per cent. acetic acid containing about one molecule of chromate of potassium to each one hundred molecules of the acid.

Loss in weight, 0.0035 gram.

Experiment D.

Weight of chromate of potassium, 0.4575 gram.

Wash liquid, 10 per cent. acetic acid containing about ½ molecule of chromate of potassium to each one hundred molecules of the acid.

Loss in weight, 0.0031 gram.

Experiment E.

Weight of chromate of barium, 0.4544 gram.

Wash liquid, 10 per cent. acetic acid containing about two molecules of chromate of potassium to each one hundred of the acid.

Loss in weight, 0.0039 gram.

Experiment F.

Weight of chromate of barium, 0.4505 gram.

Wash liquid, 20 per cent. acetic acid containing about one molecule of chromate of potassium to each one hundred molecules of the acid.

Loss in weight, 0.0039 gram.

In the experiments C, D, E and F, the loss in weight would seem to indicate that the chromate of barium had been to some extent dissolved by the acetic acid, notwithstanding the presence of the chromate of potassium. But this is believed not to have been the case. The filtrates remained perfectly clear when treated with dilute sulphuric acid, though allowed to stand in some instances more than three weeks. Moreover it was found that a single milligram of barium is sufficient to produce an immediate and persistent cloudiness in 250 c.c. of 20 per cent. acetic acid containing one molecule of chromate of potassium to each one hundred of the acid and a little sulphuric acid. The filtrates must therefore have contained in every instance less than one milligram of barium.

On examining into the other possible causes of loss in weight, it was discovered that the chromate of potassium employed contained a small quantity of sulphate, and that the filters lost weight to a slight extent when washed with ten and twenty per cent. solutions of acetic acid containing chromate of potassium. The loss from the first cause is believed to have been insignificant, since the quantity of sulphate contained in the chromate was very small, and the decomposition of the chromate of barium by a sulphate is very slow. This decomposition may, however, have been somewhat accelerated by the presence of acetic acid. The loss from the second cause may have been more considerable, since some of the papers experimented upon diminished two and a half milligrams in weight.

The experiments here recorded are to be regarded as preliminary only. The work will be resumed at the earliest opportunity. The results thus far obtained indicate: (1) That barium can be precipitated in the presence of acetic acid by an excess of chromate of potassium nearly, if not quite, as completely as by sulphuric acid; (2) That the precipitate cannot be washed with pure solutions of acetic acid, however dilute; (3) That, if a small quantity of chromate of potassium is added, the precipitate can be washed with quite concentrated solutions of acetic acid without undergoing solution. By using a wash liquid of acetic acid containing chromate of potassium it is probable that barium can be readily and completely separated from strontium, calcium and magnesium. It is reasonable to suppose that any other soluble chromate would protect the barium compound equally well; indeed it is only on the basis of such a supposition that the results reported by Frerichs can be even partially explained. He must have ceased washing with dilute acetic acid as soon as the last traces of chromate of strontium, calcium or magnesium had passed into the filtrate; for otherwise there would have been a deficiency of barium. The observation that a colorless filtrate can be obtained by washing chromate of barium with dilute acetic acid must have been erroneous.

JOHNS HOPKINS UNIVERSITY, *June*, 1880.

ON A-TOLUENEDISULPHONIC ACID AND ITS DERIVATIVES.

BY C. FAHLBERG,

Fellow in Chemistry, Johns Hopkins University.

In a previous communication[*] it was stated that when toluene-parasulphochloride is treated with fuming or concentrated sulphuric acid, α-toluenedisulphonic acid is formed. It was shown that this acid is identical with the acid obtained by Blomstrand,[†] who had prepared it in a different way. It remained to ascertain the positions of the two sulpho-groups in the acid, as its structure had not been determined. For this purpose the following investigation was undertaken.

It would be a simple matter to decide this question if toluene-orthosulphochloride should upon treatment with sulphuric acid give the same product as the para-compound in the previously described experiment. It was thought at first that Blomstrand's second product might have been derived from the ortho-compound, and was not a consequence of the high temperature at which he worked, and to which he ascribed the formation of the β-toluene-disulphonic acid. If my explanation could be shown to be true, then the attempt to solve the question proposed above would have proved fruitless. Another obstacle presented itself in the statement made by Beckurts,[‡] that the mixed toluenemonosulphonic acids

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[*] This Journal, 1, 170.

[†] Ber. d. deutsch. Ges. 5, 1084.

[‡] Ber. d. chem. Ges. 10, 943.

which had been used in Blomstrand's experiment consisted not only of two, but of three isomeric monosulphonic acids. This evidently would have complicated the investigation in question, had it not been found that Beckurts' statements in regard to the third isomer were wrong,* and that his meta-acid consisted of a mixture of the ortho- and para-acids. In regard to Blomstrand's experiment there was very little doubt that his second disulphonic acid had resulted, as supposed by himself, in consequence of the high temperature. To prove this beyond any doubt, the following experiments were performed at temperatures not exceeding 150°.

I. Almost pure, solid tolueneparasulphochloride and fuming sulphuric acid were allowed to act upon each other at a temperature of 140–150° for about three hours. After the reaction had ceased, and the hydrochloric acid had been gradually given off, the mass was diluted with water and subsequently treated with barium carbonate. The filtrate from barium sulphate gave, on evaporation, an easily soluble barium salt, which was converted into the potassium salt. The first two crops of crystals were almost pure potassium α-toluenedisulphonate. Then it became advisable to evaporate the last mother-liquor to dryness, and to wash the residue with alcohol in order to remove the unchanged potassium toluenemonosulphonate. The potassium monosulphonate is very easily soluble in alcohol, whereas potassium α-disulphonate is almost insoluble in alcohol of 93–95 per cent. On dissolving the residue on the filter in water, more potassium α-toluenedisulphonate was obtained, and not a trace of another compound, showing that Blomstrand's β-disulphonic acid had not been formed under these circumstances. An analysis of the pure toluenedisulphonate of potassium gave the following results:

I. 0.35 gram gave 0.471 gram $BaSO_4$ = 0.0647 gram S.

II. 0.33675 gram lost 0.018 gram H_2O at 200°.

III. 0.3371 gram gave 0.16725 gram K_2SO_4 = 0.0751 gram K.

		Calculated.		Found.
$C_7H_6O_6$	...	186.	53.44	
S_2	...	64.	18.49	18.50
K_2	...	78.26	22.60	22.30
H_2O	...	18.	5.47	5.31
		346.26	100.00	

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* This Journal, 1, 170.

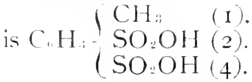
From the pure potassium salt and phosphorus pentachloride the chloride of the acid was obtained in nearly theoretical quantity. It was washed with water and recrystallized from ether. It fused at 52°.

The pure chloride treated with aqueous ammonia gave the disulphamide, fusing at 186–187°. It was noticed that the chloride is attacked with difficulty by aqueous ammonia, in consequence of which the reaction required to be facilitated by the use of a water-bath. It has been found, however, that in the formation of the amide from the chloride and aqueous ammonia the reaction is not a clean one, only 30–40 per cent. being obtained; whereas, when a strong alcoholic solution of ammonia is employed no heat is required, and a much larger yield is obtained. The amide is very soluble in an excess of ammonia, and the solution has to be freed from the excess before the amide will separate out.

The secondary reaction which was noticed in the formation of the disulphamide seems to be due to the replacement of one chlorine atom by ONH_4, and of the other by NH_2, though the analysis of the barium salt disclosed no relation with an acid of the formula $C_6H_3\left\{\begin{array}{l}CH_3\\SO_2OH\\SO_2NH_2.\end{array}\right.$ The barium salt which was analyzed can be obtained if the mother-liquor from the preparation of the disulphamide is boiled with litharge for several hours, until it ceases to give off ammonia, when ONH_4 is changed into Opb, and the NH_2 remains unaltered. On adding to the filtrate, first, sulphuric acid and then barium carbonate, a barium salt of a syrupy appearance can be obtained. This has to be separated from $C_6H_3\left\{\begin{array}{l}CH_3\\(SO_2O)_2Ba\end{array}\right.$ with alcohol, which leaves the latter undissolved. The evaporated alcoholic filtrate was dried at 150°, and of the amorphous, though not hygroscopic residue, a barium determination was made which gave 10.7 per cent. Ba. From the analysis it appears that the product is not $C_6H_3\left\{\begin{array}{l}CH_3\\SO_2Ba\\SO_2NH_2\end{array}\right.$ but a compound of different composition, containing barium and nitrogen. It is possible that an acid of the formula $C_6H_3\left\{\begin{array}{l}CH_3\\SO_2OH\\SO_2NH_2\end{array}\right.$ can be prepared from the disulphamide by boiling with hydrochloric acid, as the two sulphamide groups may show a marked difference in their conduct towards hydrochloric acid. One of the groups in the benzoic acid series can be easily changed with hydrochloric acid into a sulpho-group, whereas the same transformation does not take place in the other. The different behavior of the two groups will be discussed more fully when I come to speak of the disulpho-derivatives of benzoic acid.

II. Liquid tolueneorthosulphochloride was now subjected to the same treatment with fuming sulphuric acid at a temperature of 135°. On examining the product, however, it gave the same salts, chloride and amide, as described under I. From 100 grams of the chloride not a trace of a second acid could be obtained. It was noticed that the reaction with sulphuric acid occurred in less time, and at a slightly lower temperature. The yield was better, and the potassium salt required less washing with alcohol than in the previous experiment with the para-compound, but it was darker colored, owing to the fact that the liquid chloride is always darker than the solid sulphochloride.

It is evident from these experiments then, that the second acid of Blomstrand was not formed from orthosulphochloride at 135°, but must have been formed in consequence of the temperature, which was carried to 180° in his experiment. It is, moreover, not improbable that at this high temperature a trisulphonic acid was formed, as he made no analysis to confirm his view that a second disulphonic had actually been formed. Blomstrand also expressed the view that the toluenedisulphonic acid, prepared by C. Senhofer,* is different from his acid, but that statement requires, as I think, confirmation. It has been shown in the course of these experiments that the two monosulphochlorides, one of which belongs to the ortho and the other to the para series, yield one and the same disulphonic acid. This furnishes the proof of the structure of α-toluenedisulphonic acid, according to which the positions of the two sulpho-groups are 2 and 4 with reference to the CH_3 group. Hence the formula for α-toluenedisulphonic acid is



$$C_6H_3\begin{cases} CH_3 & (1). \\ SO_2OH & (2). \\ SO_2OH & (4). \end{cases}$$

Other confirmatory experiments to complete the proof of the structure of this acid will be given below.

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[*] Liebig's Annal. 164, 126.

Oxidation of 1, 2, 4 Toluenedisulphamide.

The amide which fuses at 186–187° was subjected to oxidation with permanganate of potassium. The following proportions were used: 1 part of the amide, 5 parts of potassium permanganate were dissolved in 100 c. c. of water. The mixture was heated on a water bath for several hours. It was found that 4 to 5 hours were sufficient to complete the oxidation. The solution was then decolorized with alcohol, filtered and evaporated to a small volume. After the addition of hydrochloric acid a colorless compound separated. It was recrystallized from water. From a saturated solution it is obtained as a fine crystalline powder, and in small rhombic plates from a dilute solution. The yield thus obtained weighed half as much as the toluenedisulphamide employed.

The fine powder and the rhombic plates were analyzed separately with the same results.

Fine crystalline powder:

I. 0.32875 gram of the substance gave 0.5905 gram $BaSO_4$ = 0.0819 gram S.

II. 0.3168 gram of the substance gave 0.5682 gram $BaSO_4$ = 0.07804 gram S.

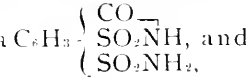
III. 0.3119 gram substance gave 29 c. c. N at 17° at 765 mm. barom. = 0.033786 gram N.

Small rhombic plates:

IV. 0.3292 gram substance gave 0.59075 gram $BaSO_4$ = 0.0811 gram S.

		Calculated.		Found.			
				I.	II.	III.	IV.
$C_7H_7O_5$	...	170	54.89				
S_2	...	64	24.43	24.66	24.63	...	24.63
N_2	...	28	10.68			10.83	
		262	100.00				

It was expected that the substance would be a compound of the same class of bodies to which Prof. Remsen and myself had ascribed the name "sulphinide."* This expectation was fully justified. The analysis corresponds to the formula



$$C_6H_3\left\{\begin{array}{l} CO \\ SO_2NH, \\ SO_2NH_2. \end{array}\right.$$

and

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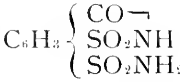
* This Journal, 1, 426.

its name is hence sulphaminebenzoic sulphinide. The same condensation has taken place here which has been noticed in a number of cases since, whenever a sulphamide group is located in an ortho position with reference to a carboxyl group. This is the more significant, as there has been no case recorded in which this law does not hold good.



Sulphaminebenzoic sulphinide, $C_6H_3\left\{\begin{array}{l}CO\neg\\SO_2NH\\SO_2NH_2\end{array}\right.$ (or paraanhydrodisulphaminebenzoic acid), crystallizes, as above described, from water. It is more easily soluble in hot water. It is difficultly soluble in cold water, and almost insoluble in cold hydrochloric acid; but if the aqueous solution is boiled for any length of time in the presence of hydrochloric acid, sulphaminebenzoic sulphinide is transformed into sulphaminesulphobenzoic acid, which will be described fully below. It is very difficult to avoid a partial change when the product obtained by the addition of hydrochloric acid is recrystallized, unless the hydrochloric acid is entirely removed by drying in the air at ordinary temperature. Alcohol and ether dissolve it very easily without change, even in the presence of hydrochloric acid. It fuses at 285° (uncorr.), but undergoes at the same time partial decomposition.

Phosphorus pentachloride does not act upon sulphaminebenzoic sulphinide, either at the ordinary temperature or when heated. This fact proves the absence of a hydroxyl group in the compound.

The aqueous solution of sulphaminebenzoic sulphinide has acid properties. When it is neutralized with different carbonates, corresponding salts can be obtained. These are salts of disulphaminebenzoic acid, $C_6H_3\left\{\begin{array}{l}COOH\\SO_2NH_2\\SO_2NH_2\end{array}\right.$. Strong acids throw down from solutions of these salts sulphaminebenzoic sulphinide, and not disulphaminebenzoic acid. The existence of the free acid seems to be improbable, as all attempts to obtain it have failed. The salts of disulphaminebenzoic acid could not be obtained in crystalline form. They all appear strongly hygroscopic, and could not be obtained in a form suitable for analysis. Lead, barium, calcium, potassium and sodium salts were prepared, but with the exception of the calcium salt were not analyzed. The analysis of the calcium salt was undertaken to prove that the salts were disulphaminebenzoates.

The ester, which crystallizes well, was also analyzed with the same object. This latter compound is best adapted for the purpose.

Calcium disulphaminebenzoate,  $C_6H_3\left\{\begin{matrix}COOca\\(SO_2NH_2)_2\end{matrix}\right.$, is obtained if a solution of sulphaminebenzoic sulphinide is neutralized with Iceland spar, and the solution evaporated to dryness. The salt appears as a syrupy mass. It loses its water at 120°, and on exposure to the moist air proves to be very hygroscopic. It is very easily soluble in hot and cold water. Alcohol dissolves it less readily, and from this solution it separates in amorphous condition. Ether does not dissolve it. Two calcium determinations were made of this salt, which gave the following data:

I. 0.472 gram of the calcium salt gave 0.109 gram $CaSO_4 = 0.032$ gram Ca.

II. 0.52 gram substance gave 0.12 gram $CaSO_4 = 0.0354$ gram Ca.

The analyzed salt was dried at 120°.

		Calculated.		Found.	
				I.	II.
$C_7H_7S_2N_2O_6$	...	279	93.31	...	...
$Ca\frac{1}{2}$	...	20	6.69	7.00	6.80
		299	100.00		

Disulphaminebenzoic ethyl ester,  $C_6H_3\left\{\begin{matrix}COOC_2H_5\\(SO_2NH_2)_2\end{matrix}\right.$, can be prepared from sulphaminebenzoic sulphinide, alcohol and dry hydrochloric acid in the ordinary way. The alcohol must be as nearly absolute as possible (repeated distillation over caustic lime is sufficient), and the hydrochloric acid must be dried perfectly to effect a complete transformation of sulphaminebenzoic sulphinide into the ester.*

After the alcoholic solution was saturated with hydrochloric acid it was evaporated to dryness. The residue was recrystallized from water, when long, beautiful needles of a silky lustre were obtained, which proved to be the desired ester. The ester is difficultly soluble in cold, more soluble in hot water. Alcohol and ether dissolve it readily. It fuses at 198–200° (uncorr.) On analysis the following results were reached:

I. 0.3146 gram substance gave 0.477 gram $BaSO_4 = 0.0655$ gram S.

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* If the same conditions are observed in the case of benzoic sulphinide the ester of orthosulphaminebenzoic acid can be obtained.

II. 0.3105 gram substance gave 26 c.c. N at 27° at 764 mm. barom. = 0.0287624 gram N.

		Calculated.		Found.
$C_9H_{12}O_6$	...	216	70.14	...
S_2	...	64	20.78	20.82
N_2	...	28	9.08	9.26
		308	100.00	

The analyses of the ester and the calcium salt were sufficient to prove that they were derivatives of disulphaminebenzoic acid. It may not be out of place to indicate a possible transformation which the ester, according to analogy, might undergo if subjected to long boiling with dilute hydrochloric acid. As indicated above, in connection with the transformation of $C_6H_3\left\{\begin{array}{l}CO-\\SO_2NH\\SO_2NH_2\end{array}\right.$ by dilute hydrochloric acid, one of the ammonia residues (that in the ortho position) can easily be converted into hydroxyl, whereas the other is unaffected by the same treatment. This suggests the possibility of transforming disulphaminebenzoic ester into an acid ester of disulphamine sulphobenzoic acid, with the sulpho-group in the ortho position and the sulphamide group in the para position. Such a transformation could not be well effected otherwise. It is possible that this transformation is not restricted to the group $\left\{\begin{array}{l}CO-\\SO_2NH,\end{array}\right.$ but that groups like $\left\{\begin{array}{l}COOC_2H_5\\SO_2NH_2\end{array}\right.$ and $\left\{\begin{array}{l}CH_3\\SO_2NH_2,\end{array}\right.$ in the ortho position with reference to each other, may give similar results.

1, 2, 4 Disulphobenzoic Acid.

If the mother-liquor from sulphaminebenzoic sulphinide is evaporated to a very small volume, potassium chloride separates out. If this operation is repeated until no more potassium chloride is deposited, the last mother-liquor yields a large amount of a well crystallized compound. This was found to contain potassium, but no nitrogen. It is a salt with a remarkable power of crystallization. The analysis of this compound gave the following results:

I. 0.3356 gram substance gave 0.45525 gram $BaSO_4$ = 0.0625 gram S.

II. 0.23655 gram lost 0.0105 gram H_2O at 180°, and gave 0.1093 gram K_2SO_4 = 0.0491 gram K.

	Calculated.		Found.
$C_7H_4O_8$	216.	56.52	...
S_2	64.	17.86	17.73
K_2	78.26	20.84	20.75
H_2O	18.	4.78	4.43
	376.26	100.00	

These figures correspond very closely with those required by a compound of this formula $C_6H_3\left\{\begin{array}{l}COOH\\SO_2OK\\SO_2OK\end{array}\right. + H_2O$, which is the acid potassium salt of disulphobenzoic acid. Its formation from toluenedisulphamide by oxidation is analogous to that of monopotassium orthosulphobenzoate from tolueneorthosulphamide. It is the same salt which Blomstrand prepared from potassium toluenedisulphonate by oxidation with potassium pyrochromate and sulphuric acid. This is noteworthy, as it can help to explain certain phenomena, noticed in the oxidation of ortho derivatives of toluene, at a later stage of this communication.

Di-potassium disulphobenzoate, $C_6H_3\left\{\begin{array}{l}COOH\\(SO_2OK)_2\end{array}\right. + H_2O$, crystallizes in large, rhombic forms from its aqueous solution. It is more soluble in hot than in cold water. In cold hydrochloric acid it is less soluble than in water. Alcohol and ether do not act upon it.

The late Dr. J. R. McD. Irby, to whom I am indebted for his kindness in examining the salt crystallographically, gave me the following statement:

System rhombic, a : b : c = 1.3483 : 1 : 1.8288.

Forms—{ 011 }—{ 101 }—{ 001 }—{ 100 }—{ 098 }—{ 1588 } { 15823 }.

He had promised to publish certain interesting crystallographical relations which he had found to exist between the acid potassium salt of orthosulphobenzoic acid and the salt here described, but was prevented from doing so by his sudden death.

The proportions in which the nitrogenous acid and the non-nitrogenous potassium salt are formed from toluenedisulphamide by oxidation are very nearly the same as in the oxidation of tolueneorthosulphamide. If it were necessary to express this action by a chemical equation, it would be similar to that given in an earlier paper* on the oxidation of tolueneorthosulphamide. The products of oxidation were formed in equal quantities.

It is remarkable that a nitrogenous acid potassium salt of the formula $C_6H_3\left\{\begin{matrix}COOH\\ SO_2OK\\ SO_2NH_2\end{matrix}\right.$ was not formed by the oxidation. At least no trace of a compound containing nitrogen and potassium could be detected. Doubtless, therefore, toluenedisulphamide and tolueneorthosulphamide act in exactly the same way towards potassium permanganate. The sulphamide group in the para position is to some extent influenced by the sulphamide group in the ortho position, at least in the oxidation above referred to. In this special case the result is that both sulphamide groups are converted into sulpho-groups.

In case of tolueneparasulphamide, we notice a striking difference. The only sulphamide group present occupies the para position, and it is much more stable than the two sulphamide groups in the compounds just described. This shows that when a second group enters the compound and takes its place in the ortho position, the stability of the former is broken and its conduct towards oxidizing agents changed. I have not prepared many salts of disulphobenzoic acid, since they have been prepared and analyzed by Blomstrand. It has, however, been found that when sulphaminebenzoic sulphinide is heated in a sealed tube with pure hydrochloric acid to 150–170°, it is completely changed into disulphobenzoic acid and ammonium chloride. This furnishes a good method for the preparation of the acid. The solution is then evaporated to dryness, and the residue heated to 200°, in order to volatilize ammonium chloride.

1, 2, 4 Disulphobenzoic acid, $C_6H_3\left\{\begin{matrix}COOH\\ (SO_2OH)_2,\end{matrix}\right.$ when recrystallized from pure, concentrated hydrochloric acid, is obtained in large, beautiful crystals, which admit of measurement. The acid is not deliquescent, and can be kept in the air without undergoing any change. It fuses above 285°. On cooling it solidifies to an amorphous, transparent mass. It is very easily soluble in cold as well as hot water. Alcohol and ether do not dissolve the acid. From the pure acid, the acid potassium salt was prepared in the ordinary way, which gave 20.50 per cent. K, the formula $C_6H_3\left\{\begin{matrix}COOH\\ (SO_2OK)_2\end{matrix}\right. + H_2O$ requiring 20.78 per cent. K. This

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* This Journal, 1, 426.

proved to be identical with the acid potassium salt obtained by direct oxidation from toluenedisulphamide.

In order to prove that when a compound containing the group SO_2Cl and the group COCl in the ortho position with reference to each other is treated with aqueous ammonia, an ammonium salt of a sulphamine acid is formed, the neutral potassium salt of disulphobenzoic acid was subjected first to the action of phosphorus pentachloride. The resulting chloride was then treated with aqueous ammonia, when nothing separated, even after long standing. If the solution be evaporated to a small volume, and be then acidified with hydrochloric acid, sulphaminebenzoic sulphinide is precipitated. Of this the disulphaminebenzoic ethylester was prepared, which fused exactly at 199°. The reaction which takes place in the formation of sulphaminebenzoic sulphinide may be represented thus: First—

$$C_6H_3\left\{\begin{array}{l}COCl\\ SO_2Cl\\ SO_2Cl\end{array}\right\} + 6NH_3 + H_2O = C_6H_3\left\{\begin{array}{l}COONH_4\\ SO_2NH_2\\ SO_2NH_2\end{array}\right\} + 3NH_4Cl.$$

Second: On treating with hydrochloric acid—

$$C_6H_3\left\{\begin{array}{l}COONH_4\\ SO_2NH_2\\ SO_2NH_2\end{array}\right\} + HCl = C_6H_3\left\{\begin{array}{l}CO\neg\\ SO_2NH\\ SO_2NH_2\end{array}\right\} + NH_4Cl + H_2O.$$

Prof. Remsen and Dr. Burney have tried this reaction on other compounds in which the two groups were in the same position, and they have obtained similar results.

Oxidation under varied Conditions.

It was noticed by Remsen and Iles* that when sulphaminemetatoluic acid is oxidized with permanganate of potassium, not sulphamineisophthalic acid, but an acid potassium salt of sulphoisophthalic acid is formed. It was found afterwards by Remsen and Coale† that if the solution is made alkaline, isophthalic sulphinide is obtained as a product of the oxidation. This difference in the result must be ascribed to the fact that in the one case an acid solution is used, while in the other the solution is alkaline. In the acid solution the NH_2 group is replaced by OH, whereas in the alkaline solution this replacement is not effected. The acid solution was

* This Journal, 1, 124.

† Ber. d. chem. Ges. 12, 1436.

weak, as the character of sulphaminemetatoluic acid will indicate. It was thought advisable to try the same experiments with tolueneorthosulphamide and 1, 2, 4 toluenedisulphamide, as the two had been shown to conduct themselves in a similar way under the influence of oxidizing agents. For this purpose the above named substances were oxidized in the following ways:

I. *In an acid solution with permanganate of potassium.* This could only be effected by adding an acid to the oxidation mixture, as the two amides under investigation are of an entirely neutral character. Carbonic acid was finally employed for this purpose. It is possible that other acids or acid salts might give the same results. In this special case carbonic acid was conducted for twelve hours through the vessel in which the oxidation was carried on. The heat of a water-bath was constantly applied. The contents were then carefully investigated. It was found that the product of oxidation was in each case not the nitrogenous acid, but the non-nitrogenous potassium salt. After the addition of hydrochloric acid the corresponding acid potassium salts were obtained. No other product was formed.

If, on the other hand, the oxidation is only carried on for three-quarters of an hour under the same conditions as just described, two products are formed; the nitrogenous compound in comparatively small quantity.

II. *In an alkaline solution with permanganate of potassium.* The same proportions of water, permanganate and the substance employed were taken as in the previous experiments. To the solution potassium hydroxide was added. The mixture was then heated on the water bath for four to five hours. The products formed by this oxidation were two in equal quantities, and the same as described before. They did not differ from those obtained by oxidation in a solution neutral at the beginning.

III. *In an acid solution with pyrochromate and sulphuric acid.* The proportions used were: 1 part of toluenedisulphamide, 7 parts of potassium pyrochromate and 10 parts sulphuric acid, diluted with three times its volume of water. After the oxidation had been carried on on the water-bath for five to six hours, it was found that about half of the amide had remained unchanged. It was filtered off. The solution was then reduced with alcohol and treated with barium hydroxide and barium carbonate. The filtrate from the above treatment proved to be strongly alkaline. The solution was evaporated to a small volume, and then hydrochloric acid was added to it. Nothing was precipitated. This proved the absence of the nitrogenous acid. From the solution, however, a small quantity of acid potassium disulphobenzoate was obtained, which proved to be identical with the salt of Blomstrand, who obtained it by oxidation from potassium toluenedisulphonate, pyrochromate and sulphuric acid. I still think that the large quantity of the unchanged amide in my experiment must have been due to the small quantity of water with which the sulphuric acid was diluted.

From the above experiments the following conclusions can be drawn:

1. That toluenedisulphamide and tolueneorthosulphamide act in the same way towards oxidizing agents.

2. That in an acid solution the products are not the same as those which are formed if the solution is neutral or alkaline at the beginning.

3. That pyrochromate of potassium and sulphuric acid (sufficiently diluted with water) have the same effect on the two sulphamides as permanganate of potassium in an acid solution, but that the yield is much smaller when the former oxidizing agent is employed, and that this must be attributed to certain causes not fully understood at present.

Action of dilute hydrochloric acid on sulphaminebenzoic sulphinide.

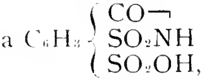
If sulphaminebenzoic sulphinide is boiled with dilute hydrochloric acid for four to five hours, complete transformation takes place. If the solution is evaporated by boiling to a very small volume, no trace of sulphaminebenzoic sulphinide is noticed, but a compound of an entirely different nature begins to crystallize out, if the solution is strongly acid.

These first crystals were recrystallized from hydrochloric acid, and subjected to an analysis, which gave the following results:

I. 0.254 gram substance gave 0.4178 gram $BaSO_4$ = 0.0574 gr. S.

II. 0.241 gram substance gave 11 c.c. N at 27° at 766 mm. barom. = 0.012175 gram N.

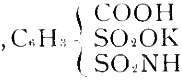
		Calculated.		Found.
$C_7H_7O_7$	...	202	72.15	...
S_2	...	64	22.85	22.60
N	...	14	5.00	5.05
		280	100.00	

The analysis shows that the compound contains half as much nitrogen and a little less sulphur than the amount required for sulphaminebenzoic sulphinide. All reactions with the compound agree for the formula  $C_6H_3\left\{\begin{matrix}COOH\\ SO_2OH\\ SO_2NH_2,\end{matrix}\right.$ according to which it is sulphamine sulphobenzoic acid, and not sulphobenzoic sulphinide of the formula  $C_6H_3\left\{\begin{matrix}CO-\!\!\!\urcorner\\ SO_2NH\\ SO_2OH,\end{matrix}\right.$ as might have been expected.

Sulphamine sulphobenzoic acid,  $C_6H_3\left\{\begin{matrix}COOH & (1)\\ SO_2OH & (2)\\ SO_2NH_2 & (4)\end{matrix}\right.$, crystallizes in large, beautiful crystals. These are not hygroscopic, and can be kept for any length of time in the air without undergoing change. The pure acid fuses at 165° without decomposition. It is so easily soluble in cold as well as hot water that it cannot be well obtained in crystalline form, unless it is left to stand for a very long time in a dessicator over sulphuric acid. It crystallizes well from hydrochloric acid, in which it is not so soluble. The same acid is formed, when the undried, first precipitated sulphaminebenzoic sulphinide is recrystallized from boiling water, as indicated above. Alcohol dissolves it slightly; ether not at all.

To prove in a more direct way that the group SO_2NH, and not the group SO_2NH_2, was changed into the sulpho-group, the following experiment was performed: Two flasks, one of which contained benzoic sulphinide, and the other parasulphaminebenzoic acid in equal quantities, were boiled for several hours with equal volumes of dilute hydrochloric acid. The contents of each flask were then examined. A marked difference was noted between the two: benzoic sulphinide was completely converted into orthosulphobenzoic acid, whereas parasulphaminebenzoic acid remained perfectly unchanged. This strengthens the proof for the correctness of the formula accepted above for sulphamine sulphobenzoic acid.

Attention was called above to the possible transformation of SO_2NH_2 (in the ortho position) into SO_2OH. The further discussion of this subject can be omitted here.

Mono-potassium sulphamine-sulphobenzoate,  $C_6H_3\left\{\begin{matrix}COOH\\ SO_2OK\\ SO_2NH_2,\end{matrix}\right.$ can be obtained, if the free acid is converted into the neutral potassium salt and this salt be treated with hydrochloric acid in excess. The first two crops of crystals are potassium chloride. On further evaporation, beautiful, transparent crystals, apparently of the rhombic system, were deposited. These contained potassium and nitrogen. They must, however, have undergone a partial decomposition, as the analysis did not agree well for a pure mono-potassium sulphaminesulphobenzoate. The salt was recrystallized several times from strong hydrochloric acid, and after each recrystallization analyzed with the following results:

I. 0.215 gram gave 0.0465 gram K_2SO_4 = 0.0208 gram K.
II. 0.2278 gram gave 0.05 gram K_2SO_4 = 0.0224 gram K.
III. 0.3015 gram gave 0.0693 gram K_2SO_4 = 0.03112 gram K.
IV. 0.2913 gram gave 0.0708 gram K_2SO_4 = 0.0318 gram K.
V. 0.3124 gram substance gave 13.5 c. c. N, at 24°, at 767 mm. barom. = 0.015125 gram N.

	Calculated.		Found.				
			I.	II.	III.	IV.	V.
$C_7H_6O_7S_2$ …	266.	83.37	…	…	…	…	…
N …	14.	4.38	…	…	…	…	4.84
K …	39.13	12.25	9.67	9.83	10.32	10.91	
	319.13	100.00					

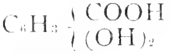
From the above analyses it appears that the substance is a mixture of the free acid and the acid potassium salt. It is very probable that the strong hydrochloric acid has effected a partial replacement of both potassium atoms by hydrogen. At all events this seems to be the most plausible explanation. The determinations of potassium and nitrogen confirm this view. The substance was not recrystallized from pure water, in which it is very soluble. A quantity of this salt is still in my possession, and I shall try to purify it, if possible, by recrystallization from water. The impure, air-dried salt fuses at about 300° without loss of weight. It is not soluble in alcohol.

Action of Potassium Hydroxide on 1, 2, 4 Disulphobenzoic Acid.

Blomstrand is responsible for the statement that potassium disulphobenzoate yields, upon fusion with caustic potash at a high temperature, only dioxybenzoic acid. This is not correct. If the fusion is conducted at a temperature above 250° for a considerable length of time the product is resorcin, and not dioxybenzoic acid; at least no trace of such an acid could be found in the fused mass. The fused mass assumes a deeply carmine red color above 250°, which is the best indication that resorcin has been formed. On dissolving and acidifying the product of fusion, ether extracted a slightly dark colored product. This proved to be very soluble in cold water. Dioxybenzoic acid is, according to Blomstrand's own statement, difficultly soluble in cold water. It could not have been the same product. The product had no acid properties. It was treated subsequently with potassium carbonate in order to remove every possible trace of an acid, and was then extracted with ether for a second time. This second ethereal extract yielded nearly pure resorcin. It crystallized well. It was sublimed, and in this condition it fused at 105° (uncorr.) It gave the characteristic blue reaction with ferric chloride. From it and phthalic anhydride, fluorescein and tetrabromfluorescein were obtained. These reactions were sufficient to identify it. The residue from the second ethereal extract was acidified with hydrochloric acid, and for a third time extracted with ether. On this occasion, however, ether extracted nothing, showing that the expected dioxybenzoic acid was not a product of this particular fusion.

Dioxybenzoic acid can be easily prepared from potassium disulphobenzoate, if the fusion is conducted at a moderate temperature, not exceeding 250°. It must be remembered that the slightest change in color is an indication of a decomposition of dioxybenzoic acid into resorcin and carbonic acid, and that this should be avoided if a large yield of the acid is the object of the fusion. It is very difficult to avoid the formation of a small quantity of resorcin. The fused mass has to be treated in the way indicated above. The first extract contains resorcin and dioxybenzoic acid together. The second, after treatment with potassium carbonate, resorcin, and the third dioxybenzoic acid, with all the characteristic properties ascribed to it by Blomstrand. It crystallizes with 1½ molecules of water, one of which it loses in the air. The amount of water found in the acid, which was dried in the air, was 5.58 per cent. H_2O. The formula $C_6H_3\left\{\begin{matrix}COOH\\(OH)_2\end{matrix}\right. + \frac{1}{2}H_2O$ requires 5.52 per cent. H_2O. Pressed between filter paper and then analyzed, it gave 14.94 per cent. H_2O. The formula $C_6H_3\left\{\begin{matrix}COOH\\(OH)_2\end{matrix}\right. + 1\frac{1}{2}H_2O$ requires 14.92

per cent. H_2O. Blomstrand states that it crystallizes from hot water with ½ a molecule of water, and from cold water with 2½ molecules of water. I find that it always contains 1½ molecules when it is pressed between filter paper, and ½ a molecule when it is dried in the air. It is very difficult to account for the difference in the water of crystallization unless we assume a typographical error in B.'s statement. He certainly did not notice the fact that the acid loses its water of crystallization at ordinary temperatures.



1, 2, 4 Dioxybenzoic acid, $C_6H_3\left\{\begin{matrix}COOH\\(OH)_2\end{matrix}\right. + 1\frac{1}{2}H_2O$, crystallizes from water in beautiful, long needles. It fuses at 194° (uncorr.). The same fusing point was noticed if the acid was first dried at 120°. It is very easily soluble in hot water, but very difficultly soluble in cold water. Its hot, saturated solution solidifies on cooling. Alcohol and ether dissolve it readily. With ferric chloride it gives a characteristic dark red color. Dioxybenzoic acid is transformed at its fusing point into resorcin and carbonic acid. On fusion with caustic potash this transformation takes place at a slightly higher temperature, but the exact temperature was not determined. This is one of the few cases in which a carboxyl group is replaced by hydrogen on fusion with potassium hydroxide.

I shall take up the study of the salts and of the different esters of 1, 2, 4 dioxybenzoic acid at the first opportunity.

The formation of resorcin escaped Blomstrand's observation, or else the structure of dioxybenzoic acid would have been determined. It not only proves now the structure of dioxybenzoic acid, but also that of all the derivatives of α-toluenedisulphonic acid. Four dioxybenzoic acids are known; of these, this is the third of which the structure has been determined. The three dioxybenzoic acids, the structures of which are known, are given below:

Names of the Acids.	Yielding	Position of Groups.
Oxysalicylic acid	Hydroquinone	1 2 5
Protecatechuic acid	Pyrocatechin	1 3 4
1, 2, 4 Dioxybenzoic acid	Resorcin	1 2 4

The position of the carboxyl group is indicated by 1.

The fourth dioxybenzoic acid is the acid prepared by Barth and Senhofer.* Of this it can only be said that the groups are, in all probability, located in the positions 1, 3 and 5, though experi-

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* Liebig's Ann. 159, 222.

mental proof has not been given up to the present. Resorcin and dioxybenzoic acid have been prepared by fusion with potassium hydroxide, from disulphobenzoic acid, sulphaminebenzoic sulphinide and sulphaminesulphobenzoic acid.

Toluenedisulphonic acid conducts itself in a different manner when fused with caustic potash. It yields: 1. Salicylic acid; 2. Paraoxybenzoic acid; 3. 1, 2, 4 Dioxybenzoic acid (in very small quantity); 4. 1, 2, 4 Isorcin; 5. Resorcin. The two last named substances could not be well separated from each other, but the presence of resorcin was detected by the fluorescein reaction with phthalic anhydride. It was, however, found that a second compound must have been present which differed in some respects from resorcin; as fluorescein was not the only product formed in the reaction with phthalic anhydride. This might have been the 1, 2, 4 isorcin of Senhofer and Blomstrand, but this cannot be said with certainty, as there is no proof of the fact.

The structure of α-toluenedisulphonic acid is proved by the following facts:

I. *Tolueneparasulphochloride* and *tolueneorthosulphochloride* yield *only one and the same toluenedisulphonic acid*, upon treatment with fuming sulphuric acid at temperatures not exceeding 150°.

II. Toluenedisulphamide yields by oxidation a *sulphinide*, which indicates that the CH_3 group and one SO_2NH_2 group are in the ortho position with reference to each other.

III. The relative position of the two sulpho-groups with reference to each other is determined by the *formation of resorcin* from all products of oxidation of toluenedisulphonic acid.

According to the above proofs the groups in toluenedisulphonic acid and its derivatives *are in the positions 1, 2 and 4.*

BALTIMORE, *June*, 1880.

REVIEWS AND REPORTS.

REPORT ON THE PROGRESS OF ANALYTICAL CHEMISTRY.

(*Continued from p. 76.*)

Hydrogen Dioxide.—A. Bertrand,[*] "On the volumetric Determination of active Oxygen in Barium and Hydrogen Dioxides." The method is based on the following reactions:

1. $BaO_2 + 2HCl = BaCl_2 + H_2O_2$.
2. $H_2O_2 + 2KI = K_2O + H_2O + I_2$.
3. $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$.

Chlorine.—G. Vortmann,[†] "Detection and Determination of Chlorine in the Presence of Bromine and Iodine." In the presence of acetic acid iodides are completely decomposed by the superoxides of lead and manganese. The former oxidizes a part of the liberated iodine to iodic acid, but not the latter. Bromides in neutral solutions are not decomposed by either oxide, and in solutions acidified with acetic acid only by the lead compound. Chlorides are not attacked by either oxide in the presence of acetic acid. Therefore, to detect chlorine in the presence of bromine and iodine, it is recommended to treat the solution with acetic acid and lead superoxide, and to boil until the solution remains colorless on clearing and no longer smells of either bromine or iodine. The bromine and a part of the iodine will have been expelled, while a portion of the latter will remain behind as iodate of lead. On filtering and washing with hot water, the whole of the chlorine free from bromine and iodine will be obtained in the filtrate.

Iodine.—E. Donath,[‡] "On a new Method of detecting and determining Iodine in the Presence of Chlorine and Bromine." Chromic acid liberates iodine from its compounds with the alkalies, but does not decompose the corresponding chlorides and bromides. The iodine thus liberated may be removed by distillation and determined in the distillate. If bromides are present the distillation must be interrupted as soon as the vapors of iodine cease to pass over, since they are to some extent decomposed when the solution becomes concentrated by evaporation.

Sulphur.—R. Fresenius,[§] "On the Determination of the Sulphur of Pyrites." The sulphur of a specimen was determined by three different persons, according to the method recommended by Fresenius,[||] which consists in fusing the finely pulverized material with a mixture of a nitrate and a carbonate of an alkali. The mean of

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[*] Bull. de la Soc. Chim. 33, 148.

[†] Berichte, 1880, 325.

[‡] Z. an. Ch. 19, 19.

[§] Z. an. Ch. 19, 53.

[||] Z. an. Ch. 16, 339.

the results obtained was 43.87 per cent. The sulphur of the same specimen was then determined by the method recommended by Lunge,* which consists in the oxidation of the material by a mixture of one part of fuming hydrochloric acid and three or four parts of nitric acid having a specific gravity of 1.36 to 1.4, evaporation with hydrochloric acid until all nitric acid is expelled, treatment of the residue with a little hydrochloric acid, filtration, precipitation of the sulphuric acid from the boiling solution with a boiling solution of barium chloride, immediate decantation through the filter, and washing—at first by decantation and with addition of a few drops of hydrochloric acid. The mean of the results thus obtained was 42.61 per cent. On heating the barium sulphate became red, and quantities of ferric oxide varying from 0.004 to 0.0085 gram were extracted. Notwithstanding the presence of the iron, the precipitates were considerably too light. On searching for the causes of the discrepancy in the results obtained by the two methods, it was found that the sulphuric acid is not completely precipitated at first when hot solutions of it, containing hydrochloric acid, are treated with a barium salt. The quantity not immediately precipitated is considerable, and greater in proportion to the amount of hydrochloric acid present. Moreover, the presence of ferric chloride hinders the precipitation.

Phosphorus.— Brunner,† "Determination of assimilable Phosphoric Acid according to Petermann." A description of the method employed by Petermann for the simultaneous determination of soluble and reverted phosphoric acid in commercial fertilizers. An appropriate weight of the material, varying from ten to two grams according as the quantity of phosphoric acid is small or large, is washed into a porcelain mortar with a solution of citrate of ammonium having a specific gravity of 1.09, gently rubbed, the suspended matter gradually poured into a 500 c.c. measuring flask, and the residue finally washed in with the citrate solution until 100 c.c. have been used. The flask is then heated exactly one hour at 35°, filled to the mark, and the contents filtered. In a measured quantity of the clear portion of the filtrate the phosphoric acid is precipitated by chloride of magnesium and ammonia, and determined as pyrophosphate of magnesium. The method yields concordant and fairly correct results.

C. Mohr,‡ "A volumetric Method of determining Phosphoric Acid in crude Phosphates and Superphosphates with Uranium in the presence of Ferric Oxide." The author proposes the following modified uranium method: From two to five grams of the finely ground material are dissolved in the heat by frequently renewed small quantities of dilute nitric acid. The several portions of liquid thus obtained are united, diluted to a known volume and filtered. A measured quantity of the filtrate is treated with acetate of sodium until a persistent turbidity is obtained, after which a quantity of the uranium solution is allowed to flow in, the liquid heated to boiling,

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* Handb. der Soda-Fabrication, 1, 92. † Z. an. Ch. 19, 141. ‡ Z. an. Ch. 19, 150.

and treated, before the complete precipitation of the phosphoric acid has been effected, with a few small grains of ferrocyanide of potassium. The phosphate of iron is decomposed with formation of Prussian blue. Care must be taken not to add too much of the ferrocyanide of potassium. Enough has been added when a drop of the liquid no longer gives the iron reaction.

Arsenic.—E. Donath,[*] "On the Decomposition of Compounds containing Arsenic and Antimony." These are frequently fused with carbonate of sodium and sulphur, and the soluble arsenic and antimony compounds thus produced extracted with water. The objection to the method lies in the fact that a large quantity of soluble sulphides is produced which, on being acidified, deposit sulphur. This difficulty may be wholly obviated by fusing with hyposulphite of sodium instead of the mixture mentioned. The hyposulphite should be previously thoroughly dehydrated and pulverized.

Potassium.—F. Muck,[†] "On the Removal of large Quantities of Potassium and Sodium Chlorides in Mineral Analyses." For this purpose advantage is taken of their insolubility in concentrated hydrochloric acid.

A. Van Hasselt,[‡] "The direct Determination of the Soda contained in Potash." The method consists in converting the carbonates into chlorides, and extracting the chloride of potassium by means of strong hydrochloric acid saturated with the chloride of sodium.

Zinc.—V. Drewsen,[§] "A new Method of determining the Value of Zinc Dust." The method consists in ascertaining how much bichromate of potassium the material will reduce in the presence of dilute sulphuric acid.

Cerium.— F. Stolba,[‖] "The volumetric Determination of Cerium." This metal may be quantitatively determined by means of potassium oxalate and potassium permanganate in exactly the same manner as calcium.

Nickel.—G. Papasogli,[¶] "Detection of Nickel in the Presence of Cobalt." If a small quantity of a salt of nickel is dissolved in cyanide of potassium and a strip of zinc brought into the solution, gas is evolved, the zinc becomes covered with a black deposit and the solution in its vicinity changes to a red color. Cobalt does not give this reaction, nor does its presence prevent it. If the platinum electrodes of a Bunsen's element are brought into a solution of potassium-nickel cyanide the same reaction appears at the negative pole. It cannot, however, be obtained by simply passing hydrogen through the solution.

Cobalt.—C. Rössler,[**] "A new Method of determining Manganese and Cobalt volumetrically." A more detailed account of the method reported in this Journal, Vol. I. page 363. The author finds that the method is applicable to the determination of cobalt

[*] Z. an. Ch. 19, 23.
[†] Ibid. 19, 140.
[‡] Ibid. 19, 156.
[§] Ibid. 19, 50.
[‖] Chem. News, 41, 31.
[¶] Berichte, 1880, 203.
[**] Liebig's Ann. 200, 323.

as well as manganese. In the presence of nickel however, the results obtained are somewhat too low.

Iron.—J. M. Eder,[*] "A new Method for the Quantitative Determination of Ferrous Oxide in the Presence of Organic Acids and Cane Sugar." If a solution of potassium ferro-oxalate is treated with an excess of silver nitrate, it is completely converted into a ferric salt while a corresponding amount of metallic silver separates out. Moreover, when a ferrous salt, whether organic or inorganic, in a solution free from mineral acid is treated with neutral oxalate of potassium, the potassium ferro-oxalate is formed, and on addition of silver nitrate the reaction just described takes place according to the following equation: $2FeO + Ag_2O = Fe_2O_3 + 2Ag$. Each atom of silver precipitated represents one atom of ferrous iron. All of the compounds except ferric hydroxide, which separate out with the silver can be removed by means of ammonia. The silver may then be dissolved in nitric acid and precipitated as chloride. It sometimes happens that the metallic silver does not readily subside. In such cases ammonia and afterwards chloride of ammonium are to be added. If a sufficient quantity of tartaric acid is present iron is not precipitated by the ammonia, and the silver may be collected and weighed as such. The best method of procedure is the following: The nearly neutral solution of ferrous salt is treated with an excess of potassium oxalate and silver nitrate and allowed to stand for some minutes. Tartaric acid sufficient to prevent the precipitation of iron is then added and finally an excess of ammonia. The precipitate of metallic silver is collected upon a filter and washed with a solution of ammonia and chloride of ammonium. Care should be taken to avoid a strong light.

Lead.—F. Lux,[†] "Volumetric Determination of the Value of Minium." Lead superoxide when treated with an excess of oxalic acid undergoes decomposition as follows:

$$PbO_2 + C_2H_2O_4 = PbO + 2CO_2 + H_2O.$$

The oxalate of lead formed by the union of the excess of oxalic acid with the reduced oxide dissolves readily in dilute nitric acid, and in this solution the undecomposed oxalic acid may be easily determined by means of permanganate of potassium. This method combined with the volumetric determination of lead by means of potassium bichromate, affords a rapid and sufficiently accurate means of ascertaining the commercial value of minium.

Alcoholic Liquors.—V. Wartha,[‡] "Contributions to the Investigation of Wine." This article treats of the detection of rosaniline compounds and of the detection and determination of sulphurous acid in wine.

L. Weigert,[§] "Detection of Salicylic Acid in Wine, &c." K. Portele proposed the following method for highly colored liquids: 100 to 200 c.c. of the fluid are treated with a solution of glue in order to precipitate the tannic acid, and then, without removing

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[*] Berichte, 1880, 502.

[†] Z. an. Ch. 19. 153.

[‡] Berichte, 1880, 657.

[§] Z. an. Chem. 19, 45.

the suspended matter, evaporated to dryness on the water-bath. From the residue the salicylic acid is extracted with ether, the extract evaporated, the acid dissolved in water and tested for with ferric chloride. In this manner one gram of the acid dissolved in a hectoliter of liquid can be detected. The author proposes as an improvement on this the following method: 50 c. c. of the material to be examined are agitated for some minutes with 5 c. c. of amyl alcohol: the alcohol, which rises to the top, is drawn off and dissolved in an equal volume of ethyl alcohol. The solution thus obtained is tested with ferric chloride.

Butter.—L. Medicus and S. Scherer,* "On the Testing of Butter." The authors commend on the basis of their own experiments the method of Reichert,† which involves the alkalimetric determination of the volatile fatty acids. They also find that melted butter does not solidify to a perfectly homogeneous mass on cooling, and that there is therefore need of some care in selecting an average specimen when butter which has been melted (Butterschmalz) is to be examined for adulteration.

Carbohydrates.—F. Soxhlet,‡ "The Conduct of Sugars towards Alkaline Copper and Mercury Solutions." The author has given in considerable detail the results of an extended and carefully conducted examination of Fehling's, Knapp's and Sachsse's methods for determining sugar. The three were investigated with reference to their application to inverted cane, grape and milk sugars, also lactose and maltose. His conclusions are, in general, 1. that each of these substances has a different reducing power for Fehling's solution: 2. that the relation between copper reduced and sugar decomposed is not constant, but depends on the concentration of the solutions and on the amount of copper in solution, or perhaps on both of these factors at the same time; 3. that the methods of Knapp and Sachsse have no advantages over that of Fehling in respect to accuracy, certainty or convenience.

Alizarine, &c.—E. Schunck and H. Roemer,§ "On the Detection of Alizarine, Isopurpurine and Flavopurpurine." These three substances give such characteristic reactions that their separate detection is a matter of no difficulty. The opposite is true when they occur as mixtures. A complete separation is very difficult, and impossible with small quantities of material. The reason of this lies in the similar conduct of all three towards most solvents, and in the fact that the characteristic reactions are in the main those of color. The separation can, however, be effected by means of fractional sublimation, that of alizarine from the other two quantitatively and with ease, that of isopurpurine from flavopurpurine with greater difficulty. Alizarine begins to sublime at 110°, flavopurpurine at 160°, and isopurpurine at 170°. The last two may be easily identified in the sublimate; since isopurpurine sublimes in the form of stout and quite perfect crystals, which appear to

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* Z. an. Chem. 19, 159.
† Ibid. 18, 68.
‡ Jour. f. pr. Ch. 21, 227.
§ Berichte, 1880, 41.

belong to the rhombic system; flavopurpurine, on the other hand, in the form of reddish-yellow needles. Moreover, the two may be separated by means of benzene, in which the former is nearly insoluble and the latter quite soluble. The apparatus used consists of two glass plates separated by a ring of lead a few millimeters in thickness.

Urea.—E. Pflüger,* "On the Quantitative Determination of Urea." The quantity of urea obtained by Liebig's method, as usually conducted, is too small. This defect may be remedied by adding at once nearly the whole amount of the nitrate of mercury required by the urea, neutralizing, and finally adding enough more of the mercury solution to give the end reaction. The author also finds it necessary to alter somewhat the correction proposed by Liebig for solutions containing less than 2 per cent. of urea.

A. Fauconnier,† "On the Determination of Urea by Alkaline Hypobromites and Hypochlorites." In view of the dispute between Mehu and Esbach with reference to the influence of sugars on the liberation of nitrogen from urea by these reagents, experiments were made upon standard solutions of urea, two of which contained a known quantity of grape sugar, and a third a known quantity of cane sugar. From the solutions containing the grape sugar very nearly the theoretical amount of nitrogen was obtained, while in the case of that containing the cane sugar there was the usual deficit. The author concludes, from some experiments made by him, that the $\frac{3}{37}$ of nitrogen not liberated when urea is treated with hypobromite undergoes oxidation to nitric acid, and that grape sugar is able to reduce this with liberation of the nitrogen.

Jay‡ finds, on the contrary, that the presence of cane sugar does increase the volume of gas liberated; though, in order to obtain the theoretical amount it would be necessary to add a quantity of the sugar equal to about two hundred and sixty-five times that of the urea. No gas is evolved during the time ordinarily required for a determination of urea when a solution of pure cane sugar is treated with hypobromite, yet the author does not believe that the additional quantity of gas obtained when this sugar is present in the solution of urea is due to a more complete liberation of nitrogen.

H. N. MORSE.

REPORT ON PROGRESS IN PHYSIOLOGICAL CHEMISTRY.

The science of physiological chemistry treats of the chemistry of the body. It is not merely a description of the proximate principles composing the different tissues and fluids of the body, but includes the more important study of the chemical processes and chemical changes taking place during life; it is the development of events by chemical processes in the body. But the more elevated bio-chemistry is dependent in great part upon the facts of zoo-

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* Berichte, 1880, 780. † Bulletin de la Soc. Chim. 33, 102. ‡ Bulletin, 33, 105.

chemistry for its theories. Before we can understand the action of any particular substance in the body we must know its composition, and in order to understand its relation to some more complex substance from which it may possibly be derived we must know its constitution. The science of organic chemistry in its rapid development has taught us much of the constitution of complex organic matter. and it is in this manner that physiological chemistry derives most benefit from zoo-chemistry. By means of the facts which it teaches we are enabled to trace to a common origin many simple bodies resulting from chemical metamorphosis in the body, and so of late much time has been spent in studying certain forms of organic matter of special importance physiologically, in order to better understand their breakings up in the animal body.

Within the past few years the decomposition of albumin under varying conditions, and by the agency of different chemical agents, has been carried on extensively in the hope of ascertaining something in regard to the constitution of this complex substance. Of great importance chemically and physiologically, it has long resisted the efforts of investigators to unravel its complicated structure, and physiologists have long been puzzled to account for the many and diverse forms of decomposition-products resulting from its splitting up in the animal body. Not yet can we consider the matter thoroughly understood, but the investigations of the past few years have thrown so much light upon the subject that our knowledge is considerably broadened.

It has been a prevalent opinion that the albuminous substances must stand somewhat intimately related to the carbohydrates, on account of the fact that the products of fermentation or decomposition of both substances were found to be closely related if not identical; and when it was discovered that by the action of bromine on glucose,* dextrin, and other carbohydrates, new and peculiar bodies having the properties of acids were formed, a way appeared to be opened for the solution of the problem of the chemical relationship of the albumins and carbohydrates. Thus, in 1871, Hlasiwetz and J. Habermann† undertook, by a series of qualitative and quantitative experiments, to ascertain if it were possible by the oxidation of different forms of albumin with bromine to obtain the peculiar acids formed by the oxidation of glucose and dextrin under similar circumstances, viz: gluconic and dextronic acids. Egg-albumin, casein and other forms of albumin decomposed by heating in a closed vessel with bromine, all agreed in giving aspartic, oxalic and carbonic acids, together with leucin and a considerable quantity of brominated compounds, but no trace of gluconic, dextronic or glycollic acids were obtained, and strange to say no tyrosin was found. Thus these investigators were not able to find direct proof of the pre-existence of carbohydrates in the albuminous matters as would have been evidenced by the finding of gluconic or other allied acid.

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* Annalen der Chem. u. Pharm. 155, 1 ; 162, 297.

† Ibid. 159, 304.

Still imbued with the idea of a probable relationship between the two classes of matter, they accounted for the absence of gluconic acid by the readiness of its decomposition into carbonic, oxalic and bromacetic acids, together with bromoform; while the absence of tyrosin was accounted for on the strength of Städeler's statement that tyrosin, by the action of chlorine, is completely changed into chloranil and chloracetone, so that it would apparently follow that bromine would act in the same manner with formation of bromanil and bromacetic acid; both of which were found, the latter in considerable quantity. Thus their decomposition of albuminous matter in this manner, though failing in the desired object, showed the presence of bodies which arranged themselves naturally into two well defined groups, the fatty and aromatic; as had also been found by investigators preceding them, but using different methods of oxidation; while a glance at the individual bodies formed shows that the highest members contain not more than six atoms of carbon in the principal radical—leucin $C_5H_{10}\left\{\begin{matrix}NH_2\\COOH\end{matrix}\right.$.

Thinking that a more careful oxidation might show the wished for bodies, Hlasiwetz and Habermann* in 1873 tried another series of experiments, using in one case hydrochloric acid and zinc chloride as the decomposing agent, and in another case dilute sulphuric acid. But in these experiments likewise they failed to find the characteristic acids formed by the oxidation of carbohydrates, obtaining simply the remote decomposition-products acetic acid, oxalic acid, etc., which, together with other bodies formed, are likewise products of the decomposition of carbohydrates. As nearer decomposition products, however, by hydrochloric acid and zinc chloride, they obtained from casein, aspartic acid, the previously discovered (by Ritthausen) glutamic acid, also leucin, tyrosin, together with some phosphoric acid, sulphuric acid and always ammonium chloride, likewise a new hydrochloric acid compound of glutamic acid, but no trace of sugar-like bodies was found nor characteristic derivatives of the same. Thus according to these authors' conclusions certain nearest or primary decomposition-products are always formed, and then besides a whole series of similar ones which are secondary, so that as characteristic for albuminous matter we have only the highest members, leucin, tyrosin, aspartic acid and glutamic acid: all the remaining are products common to both albumin and carbohydrates, and when formed from albumin may be considered as descendants of the higher members, leucin, tyrosin, etc. So the old theory of the relationship of these two classes of matter has apparently received its death-blow by these carefully conducted experiments, and although later investigators have obtained in the oxidation of albuminous matter peculiar sugar-like bodies, still nothing has been brought forward to overthrow the now generally accepted belief in the independent position of the albumins and carbohydrates.

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*Annalen der Chem. u. Pharm. 169, 150.

In 1875 Schützenberger* commenced a series of investigations upon the chemical constitution of albuminous matter, and the importance of his results is in great part dependent upon the fact that he was able to obtain a complete decomposition of the albumin, and also on his careful determination of the quantities of the different decomposition-products. He also tried the action of boiling dilute sulphuric acid on albumin with entirely new results. The plan of procedure in this latter case was to take a portion of moist coagulated albumin corresponding to one kilogram of the dry substance, mixing this with about 8 litres of water containing 200 grams of concentrated sulphuric acid, and boiling the mixture during 1½ to 2 hours; at the end of which time the mass was cooled and filtered, the residue being washed thoroughly with water until the washings were no longer acid.

The insoluble portion appears much like silicic acid or alumina, being white in color, flocculent and homogeneous, and on being dried is found to weigh always about one half the original amount. When dried it is devoid of taste, slightly yellow in color, with very weak acid reaction, insoluble in water, alcohol and ether. Thus it is found that boiling dilute sulphuric acid resolves the albumin molecule into two equal parts, of which one is soluble and the other insoluble. The insoluble portion so prepared is called hemiprotein, a substance which combines with acids and bases, forming soluble compounds, and can be purified by solution in soda, reprecipitated by exact neutralization with hydrochloric acid and washed thoroughly with water and alcohol. Prepared in this manner it contains a small quantity of sulphur, but on combustion does not leave even a trace of ash, and dried at 110° gives as an average result C 53.60, H 7.19, N 14.45 per cent. Hemiprotein boiled a longer time with dilute sulphuric acid passes slowly into solution with formation of a new substance, which is amorphous but of a slightly sweet taste, soluble in water and alcohol. This substance, called hemiproteidin, formed from hemiprotein together with leucin, tyrosin, and their homologues, gives by analysis results which lead to the empirical formula $C_{24}H_{42}N_6O_{12} + H_2O$.

The original sulphuric acid solution filtered from the hemiprotein, and containing matter corresponding to the second half of the original albumin, contains a large proportion of an amorphous substance called hemialbumin, of a very weak acid reaction, and giving by analysis the formula $C_{24}H_{40}N_6O_{10}$. Hemialbumin makes up by weight the greater part of the substances isolated from the sulphuric acid solution, and its relation to hemiproteidin is shown by the following formulae:

$$C_{24}H_{40}N_6O_{10} + O + H_2O = C_{24}H_{42}N_6O_{12}.$$

In the sulphuric acid solution was also found an acid precipitated by lead acetate and having the formula $C_{24}H_{40}N_6O_{13}$, also a body free from nitrogen, which reduced Fehling's solution vigorously,

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* Bulletin de la Société chimique de Paris, 1875–76.

and which is probably glucose or a similar body, also another body which had all the properties of sarkin.

Schützenberger has, however, obtained a more complete decomposition of albumin by boiling with barium hydroxide. He first observed that moist coagulated albumin treated with a solution of barium hydroxide in the cold was gradually dissolved and finally evolved ammonia, and that if the mixture was heated, the solution took place more rapidly with an abundant evolution of ammonia, and that, finally, the clear solution gave a granular precipitate consisting principally of barium carbonate. He found that even 120 hours' boiling of the albumin with barium hydroxide was not sufficient to break up the albumin molecule completely. As products of such a partial decomposition, however, he found, together with a large quantity of crystalline substances, a non-crystalline body, which in its reactions and composition was similar to hemiproteidin, and this substance heated to 150° with barium hydroxide decomposed in its turn with formation of carbonic acid and ammonia. In order to obtain a complete decomposition it was necessary to heat the albumin in a sealed iron flask at 150–200° for 4–6 days. By heating for a shorter time intermediate products were obtained, and these by longer treatment were converted into simple compounds.

Thus in three different experiments where albumin was heated 120 hours at 100°, 24 hours at 150°, and 8 days at 150°, with barium hydroxide, a row of decomposition-products, partly old and partly new, were obtained, and by a careful determination of their quantity much that is of importance has been learned.

By a determination of the nitrogen evolved as ammonia by heating with barium hydroxide solution, it was found that similar kinds of albumin yielded a corresponding amount; thus blood-, muscle- and plant-albumin furnished 4.3–4.8 per cent. N, egg- and serum-albumin 3.9–4 per cent. N, casein and hemiprotein 3.5–3.6 per cent. N, while ossein and gelatin yielded only 2.55–3.00 per cent. N. An examination of the precipitate obtained by heating albumin with barium hydroxide as in the previous cases, revealed the presence of carbonic, oxalic and sulphurous acids, and occasionally when the albumin was not quite free from fat, baryta soap. It is a noticeable fact that the proportion by weight of the free obtained nitrogen stands very close to the thrown off carbonic and oxalic acids, and according to Schützenberger's views, the carbonic acid and ammonia may originate from the decomposition of urea and oxamide, these two groups presumably being contained in the albumin molecule. Thus from 100 grams of casein were obtained,

17.5 grams $BaCO_3$
7.6 " BaC_2O_4
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25.1

Nitrogen corresponding to the oxalate calculated according to the decomposition equation of oxamide is 2.17, and nitrogen corresponding to the carbonate calculated according to the decomposition equation of urea is 1.08. Total nitrogen calculated for the 25.1 grams of precipitate is thus 3.25, while the nitrogen found was 3.54, making a difference of only .29. A number of similar experiments with different kinds of albumin all gave the same results. While the results thus show that the relation of the nitrogen to the baryta precipitate is a constant one, the experiments also show that the composition of the baryta precipitate in regard to the proportion of oxalate to carbonate is very variable. This fact is explained by the theory that the oxamide group $C_2O_2 \left\{ \begin{matrix} NH_2 \\ NH_2 \end{matrix} \right.$ may represent in part the urea group $CO \left\{ \begin{matrix} NH_2 \\ NH_2 \end{matrix} \right.$ similarly as in feldspar the alkali metals mutually represent or replace each other in variable proportion, or by the theory that the albumin is made up of two albuminous bodies, of which one may be a derivative of urea, the other of oxamide, the two being united in variable proportion.

While the quantities of acetic acid formed from the different kinds of albumin were found to be quite close in their agreement, tyrosin was found in widely differing quantities.

			Grams.
Tyrosin formed from 100 parts		albumin,	2.03
"	"	casein,	4.12
"	"	hemiprotein,	2.20
"	"	blood-fibrin,	3.20
"	"	plant-fibrin,	2.00

In addition to tyrosin, leucin, etc., a number of new bodies hitherto unknown as decomposition-products of albumin were discovered, viz.: crystalline amido-acids of the general formula $C_nH_{2n}NO_2$, butalamine, alanin, amidovalerianic acid; 2dly, amido-acids of the aspartic acid series $C_nH_{2n} - NO_4$. In addition to aspartic acid and glutamic acid, $C_5H_9NO_4$, a monobasic amido-acid crystallizing in glistening prisms, was found having the formula $C_5H_7NO_3$, and called glutimic acid; a body of quite interesting properties, but formed only in small quantity, 1 kilo. albumin yielding but 1.5–2 grams. Several crystalline bodies having a sweet taste were found in considerable quantity, and from their peculiar properties were called leucein and *a* and *b* gluco-protein. These three bodies differ from the amido-acids of the series $C_nH_{2n} + NO_3$, simply through a smaller content of hydrogen, and appear to be compounds of leucin or its homologues with amido-acids, poor in hydrogen, as is evidenced by the action of dilute sulphuric acid, which forms from either of these bodies sulphate of leucin and an acid of the acrylic acid series. In this case also, as in the decomposition of albumin with dilute sulphuric acid, a small quantity of non-nitrogenous substances similar to dextrin and glucose was obtained.

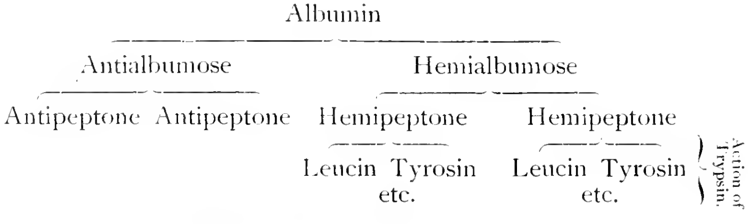
Schützenberger finally arrives at the conclusion that albumin is a complex ureid which contains about one-fifth of its nitrogen in the form of urea, and that in the decomposition of albumin with barium hydroxide the albumin molecule $C_{72}H_{112}N_{18}O_{22}S$ loses two molecules of urea, one molecule of acetic acid, one atom of sulphur, and takes up sixteen molecules of water.

$$C_{72}H_{112}N_{18}O_{22}S + 16H_2O = 2CN_2H_4O + C_2H_4O_2 + C_{68}H_{132}N_{14}O_{34} + S.$$

The formula $C_{68}H_{132}N_{14}O_{34}$ can be decomposed as follows: Into three molecules of glutamic or aspartic acid, which quantity actually corresponds to the baryta not precipitated by carbonic acid; and secondly, into a mixture of equal molecules of amido-acid of the composition $C_nH_{2n} + NO_2 + C_nH_{2n} - NO_2$.

In 1876 Kühne* published a paper on the digestion of albumin which has attracted considerable attention, the views expressed therein being generally accepted, and even now appearing in one of the more forward text-books of the science. Taking advantage of Schützenberger's work, he has arrived at a clear conception of the breaking up of albumin by the digestive fluids, and brought into line many scattered bodies which have hitherto stood by themselves without any apparent relationship to each other or to the original albumin. Thus the *a*, *b* and *c* peptones of Meissner, and the syntonin, parapeptone and dyspeptone, so variously described, are all accounted for, and their derivation and relationship clearly pointed out. Kühne considers the albumin molecule to contain two residues, one of which he calls the anti- the other the hemi-residue.

Now by the digestion of albumin with pancreatic juice, for example, the trypsin transforms the albumin completely into peptones which are not exactly alike; the anti-residue has given antipeptone while the hemi-residue has yielded hemipeptone, the two differing from each other in the fact that the antipeptone is not capable of further change, that is, trypsin or pepsin is not able to alter it further, while the hemipeptone is changed by the further digestive action of trypsin in toleucin, tyrosin, and from the recent experiments of Salomon and Chittenden into hypoxanthin and xanthin. Thus in the digestion of albumin there are two stages: in the first the albumin is converted into peptones; in the second, one-half of the peptones (hemipeptone) is further decomposed while the antipeptone remains unchanged. Following is Kühne's scheme of the decomposition of albumin by digestion:



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* Verhandl. Naturhist. Med. Verins. Heidel. 1876.

Before the anti- or hemipeptones are formed, however, intermediate products appear which correspond to bodies already known; thus as preliminary to antipeptone, antialbumose is formed, which has long been known as syntonin, while as preliminary to hemipeptone we have hemialbumose, which has long been described by Meissner as *a*-peptone. These intermediate products are arranged by Kühne in schedule form as follows:

Albumin.

Anti-group	Hemi-group
Antialbumid (Hemiprotein)	
Antialbumat (Parapeptone)	
Antialbumose (Syntonin)	Hemialbumose (*A*-peptone)
Antipeptone	Hemipeptone

Schützenberger's insoluble hemiprotein, which Kühne calls antialbumid, is wholly insoluble in gastric juice, but is soluble in dilute soda solution, and in that condition is readily digested by trypsin. At the end of the digestion nothing is precipitated by neutralization, and no trace of leucin or tyrosin can be detected, only antipeptone. Kühne's antialbumat has long been known as Meissner's parapeptone, a body formed by digestion in the presence of an insufficient quantity of pepsin, and which probably is never a product of normal digestion.

The antialbumat, as Meissner has previously said of parapeptone, is soluble in gastric juice, but not digestible, while by trypsin it is readily digested with formation of antipeptone. By the long continued action of dilute acid on the antialbumat it is converted into the much more difficultly soluble antialbumid, which has previously been described by Meissner as dyspeptone, a body totally insoluble in acid of the strength of the gastric juice, but readily dissolved by dilute alkali, and like its fellows converted into antipeptone by trypsin.

Antialbumose or syntonin is found in the so-called neutralization precipitate, obtained from digestive fluids of good strength, but when the digestion has not been completed. In solubility and in reactions antialbumose does not differ from syntonin, neither as regards its digestibility in gastric juice, but on testing the peptones formed towards trypsin it is found that they are unalterable; in other words they are antipeptones.

The typical substance of the hemi-group, and which Kühne calls hemialbumose, corresponding to Schützenberger's hemialbumin, can be formed, as already described, by the decomposition of albumin by acid; it is also found normally in an incompleted pepsin digestion. Thus according to Schützenberger's method of decomposition, after the removal of the hemiprotein a clear fluid is obtained which, on neutralization with ammonia, fails to give any precipitate whatever. By evaporating this fluid and extracting the residue with alcohol, which takes up considerable leucin, a residue remains which dissolves readily in a small quantity of hot water, and on cooling separates out again as a snow-white powder. This is the substance which Kühne calls hemialbumose, a substance which can always be obtained with a considerable degree of purity, but only in small quantity as it is readily decomposable. Hemialbumose is difficultly soluble in cold water, easily in hot water; it is precipitated in the cold by nitric acid, dissolving in slight excess with a deep yellow color. Acetic acid and potassium ferrocyanide give a heavy precipitate, while alkali and cupric sulphate give an intense red color. In 10 per cent. salt solution hemialbumose is soluble, and forms when in sufficient quantity a jelly-like mass which, when laid in water, appears white and opaque. In dilute alkalis and acids hemialbumose is readily soluble, and is precipitated by neutralization only so far as the quantity of salt formed will allow. By pepsin and by trypsin hemialbumose is very readily changed; the body formed being in both cases hemipeptone, which, by trypsin digestion, is further decomposed into leucin, tyrosin, and other decomposition products. Hemialbumose is without doubt the same body described by Meissner as *a*-peptone, and everything tends to show that in the case of a weak digestive mixture it would not fail to be present, for Kühne says that when a digestion is broken into early large quantities can be detected, while traces have been found even after sixteen hours' digestion with a large excess of pepsin and a large quantity of acid.

Thus in the digestion of albuminous matter it is plain that by the first step in digestion the albumin molecule is resolved into its two parts, the gastric juice then readily changing the hemialbumose into hemipeptone, while the anti-group appears less susceptible to the action of pepsin, only a small portion of this group being changed into antipeptone, while the larger part, under the influence of the dilute acid, appears to be converted into partially insoluble products; but on reaching the intestinal canal these insoluble bodies, under the influence of the alkaline solution of trypsin, pass readily into solution and are digested with formation of antipeptone, which is readily absorbed, while the hemipeptone is further changed into crystalline decomposition-products.

R. H. CHITTENDEN.

DR. JUL. POST. GRUNDRISS DER CHEMISCHEN TECHNOLOGIE. Berlin. Oppenheim. 1877 and 1879.

This work, as the author states in his preface, is intended to serve as a text-book for industrial chemistry comparable in aim and scope with the manual of Wöhler and Fittig for general chemistry, to be short, but as far as possible complete, and adapted for use in teaching.

The first half, published in 1877, discussed the fabrication of crude products, the materials for further treatment, though sometimes directly used; the second half, which appeared in the latter part of last year, is occupied with the fabrication of final products, such as pass into immediate consumption. The arrangement is based, not mainly upon the chemical relationship or analogy of application of the individual products turned out, but rather upon the general character and grouping of the crude materials obtained from natural sources and of the industries based upon these, the history of each industry being worked out to its principal and subsidiary results. While this plan is a sound one on which to base a treatise upon chemical technology, it renders the discussion of some parts of the subject rather complicated, and, in view of the various ways in which processes are often combined in different manufacturers' hands, it necessitates frequent partial repetition and many cross references. In some instances the arrangement involves defect of logical order, as in the case of coal tar, the distillation and utilization of which are taken up before an account has been given of its production in connection with the manufacture of illuminating gas.

A good idea, but ill carried out, is that of a preliminary chapter on the general methods of chemical work on the great scale, such as crushing, grinding, solution, precipitation, filtration, distillation, the purification of water for technical use, the production and application of heat and cold, &c. This chapter is, however, very incomplete. For example, neither here nor in connection with the subject of the working of metallic ores, is any satisfactory reference even made to the means of subdividing and pulverizing hard materials, and such generally important processes as fractional precipitation and fractional distillation are left undiscussed.

Throughout the work the most prominent fault is the meagreness of detail with which mechanical appliances and methods are treated, while these, upon which the success or failure of a process often depends, cannot rationally be ignored or separated from the chemistry of the subject. In the explanation of the mechanical features of most great industries good figures are indispensable; those in this work vary in style of engraving, are often on too small a scale to be intelligible—*e. g.* the figures of coal-gas and sulphuric acid works — and their number is quite too small for adequate illustration of the subject. On the other hand, useful tabular schemes are often introduced to show at a glance the various stages and results of the more complicated manufactures, as of the dry distillation of lignite for paraffine, the treatment of copper ores, the treatment of mixed argentiferous ores at Freiberg, the English mode of working burnt pyrites, the crystallization of the potash salts of the Stassfurt beds, the manufacture of aniline red by means of arsenic acid, &c. Some other tables of this kind might have been added with advantage, as in illustration of the distillation of petroleum.

Some few inaccuracies of statement have been allowed to creep in; thus we are told that gold is "next to platinum," the most malleable of metals, but in general the author well supports the German reputation for care in avoiding manifest errors of pen or press. The book is largely characterized by over condensation of abundant and well collected material. There are some instances of want of due proportion in the treatment of different subjects, such as the devotion of 12 pages to gelatine and glue, while but 10 pages are allotted to the whole manufacture of sulphuric acid. Some of the industries based upon organic material—*e. g.* the treatment of fats, fermentation, and the manufacture of organic dye-stuffs of artificial origin—are discussed better and with more fulness than in the older text-books.

On the whole, the work is to be viewed as a syllabus or set of condensed notes, such as might be taken by an intelligent student during a course of lectures on chemical technology, rather than as a self-explanatory handbook for independent study or general reading. Thus considered it has real merit, and to the moderately advanced student who has access to other sources of information, or to the intelligent manufacturer who wishes for a general survey merely of other chemical industries than his own, it will undoubtedly be useful. J. W. M.

J. GIRARDIN. LEÇONS DE CHIMIE ÉLÉMENTAIRE APPLIQUÉE AUX ARTS INDUSTRIELS. 6ième édition. 5 Vol.; augmentée d'un Supplément. Paris. G. Masson. 1880.

This work differs greatly in its plan from that of Dr. Post, reviewed above, though treating of the same subject, and will suit the purposes of a different class of readers, or in the same hands each may in large measure serve as the complement of the other. M. Girardin, director of the *École Supérieure des Sciences* of Rouen, has aimed at the production of a treatise, less condensed than that of Post, but still of moderate size, and, considering the form in which it is sent out from the press, very moderate in price; adapted to general reading on the part of those who have no special knowledge of the subject previously, and particularly suited for the use of the class of intelligent *ouvriers* of whom France may well be proud, and upon whose continued existence and improvement depends so largely her material prosperity.

The general arrangement of the work is based upon a gradually developed sketch of the simpler principles of chemistry, and of descriptive chemistry; the first volume being devoted to the non-metallic elements, the second to the metals, the third and fourth to vegetable and the fifth to animal materials; while the supplement contains in the same order the results of the more recent discoveries and improvements, along with that most useful feature, often wanting in French books, a copious index to the whole.

In each chapter the substances prominently, almost exclusively, described are those utilized on an industrial scale, and the usual method for the production of each substance, its character and uses, are explained with much of the lucidity and elegance of style which distinguish French scientific writers.

While the author, bearing in mind for whom he writes, has avoided as far as possible the use of symbols and much reference to the atomic constitution of bodies, especially in the earlier portions of the book, thus marring it for the scientific student, it is a pity that, so far as such matters have been touched upon at all, the atomic weights and unitary formulæ now so generally in use have not been employed instead of the old equivalents ($C=6$, $O=8$, etc.,) and the binary mode of representing salts and the like.

On the side of the detailed industrial treatment of each substance, moreover, for the greater part only a general description is given of the most usual procedure ; variations of method, even when important, being but briefly referred to or not mentioned at all, and in some instances, which would have admitted of the incorporation of notable improvements with the general description—*e. g.* the Glover tower in the manufacture of sulphuric acid—such improvements have been passed over in silence.

A minor but specially interesting feature of the book is the fulness of the historical notices prefixed to most of the accounts of chemical processes and their products, including often biographical details in reference to the men who have been conspicuous in the development of each industry. Many little-known facts are to be found recorded in these sketches, particularly in regard to the history of industrial progress in France—as, for example, notice of the part played by the English Jacobin, Holker, after his flight to France, in the development of the sulphuric acid manufacture of the 18th century in his adopted country; of the relation of his grandson, Jean Holker, to the same industry in the days of the first Empire: of the success of Delessert, under Chaptal's auspices, in the production on a commercial scale of beet-root sugar, etc.

More than fourteen hundred good, clear woodcuts, many of them designed with much taste, serve to illustrate the book, and among these some have been chosen with an eye to the picturesque local surroundings of a manufacture which adds much to the suggestiveness of the description. Thus, under sugar, we have a view of the interior of an old-time Martinique sugar-mill with vertical wooden cylinders for crushing the cane, and under natural dye-stuffs two views of an indigo factory on the Coromandel coast. There are also inserted a number of well-selected specimens of dyed fabrics in silk and other goods and of printed cotton cloth.

The work is one of popular character, but it is essentially a very good example of what a popular scientific book should be. A very fair course of elementary reading for a student of industrial chemistry might consist of the treatises of Girardin, v. Wagner, and Post, taken up in the order in which they are here named.

J. W. M.

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RAINS, G. W. Chemical Exercises in Qualitative Analysis for Ordinary Schools. New York: Appleton. 50 cts.

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VALENTIN, W. G. A Course of Qualitative Chemical Analysis. Revised and corrected by W. R. Hodgkinson. London: Churchill. 7s. 6d.

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GRIESHAMMER, O. Einwirkung von Brom auf Rohrzucker.

HOERMANN, G. Beitrag zur Kenntniss der Pyro- und Meta-Arsensäure, sowie einiger Salze derselben.

LIVAS, A. Beiträge zur chemischen Analyse der Gesteine.

STAUB, A. Die Bestandtheile des Lorbeeröls.

VALENTINER, F. Ueber Nitro- und Amidoverbindungen der Halogenderivate des α-Cymols.

ZEITLER, J. N. Ein Beitrag zur Kenntniss der Löslichkeit der Alkalisalze in Alkohol.

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FÖRSTER, K. F. M. Ueber die äthylirten Orthoamido-Phenetole und Orthoamido-Phenole.

ROTH, C. Ueber ein neues Dibromphenol und ein Nitroderivat desselben.

LEIPZIG.

LEUCKART, R. Ueber Aethylharnstoff und einige seiner Derivate.

PRAETORIUS-SEIDLER, G. Zur Kenntniss des Cyanamids.

SAARBACH, L. Ueber die Einwirkung von Phenolen auf halogensubstituirte Fettsäuren.

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AMERICAN CHEMICAL JOURNAL.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.*

By WOLCOTT GIBBS, M. D.
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(Continued from Vol. I, p. 217.)

Phospho-Tungstates.

The phospho-tungstates, as already stated, were discovered by Scheibler, who gave provisional formulas for several different compounds. As the German chemist has published nothing farther upon the subject for six years, and as the study of these compounds seemed to be a necessary preliminary to that of other complex inorganic acids, I have devoted much time and labor to them. The investigation has proved very difficult and tedious, but has yielded results which, if not in all cases perfectly definite and conclusive, are yet as I think valuable and interesting. The difficulties met with in the study of this class of salts are in some respects analogous to those which present themselves in the case of the alkaline tungstates. They are mainly as follows:

1. The normal alkaline phospho-tungstates are readily decomposed by water, yielding acid salts which are often very complex. These acid salts are very slightly soluble, and cannot in general be

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recrystallized for analysis. They are formed in greater or less proportion whenever we attempt to purify the neutral or less acid salts by recrystallization. In many cases the ratio of tungstic and phosphoric oxides in the neutral salt is changed when the acid salt is formed, so that we can draw no certain conclusion from the constitution of one salt as to that of the other. It is usually very difficult, or even impossible, to pass from the acid back to the primitive normal or neutral salt, because the addition of an alkali produces new compounds.

2. It is difficult by any analytical method which has been devised to determine the percentage of phosphoric oxide with great accuracy, and very small differences—often not exceeding 0.2 per cent.—are sometimes sufficient to change the ratio between the number of atoms of phosphoric and tungstic oxides. In the case of tungstic oxide the divisor which we must employ ($WO_3 = 232$) is so large that a very sensible variation in the percentage of the oxide does not sensibly affect the quotient. It is consequently sometimes difficult to decide between formulas in which, for example, the ratios of the two oxides are as 24 : 1, as 22 : 1, or as 20 : 1.

3. For similar reasons it is very difficult to recognize mixtures of different salts.

4. The alkaline phospho-tungstates are usually efflorescent—frequently to a remarkable degree.

5. The salts of the different series agree so closely in physical and chemical properties that, as in the case of the tungstates, distinctive tests are not to be found.

6. It is almost impossible to predict what compound will be formed when tungstates and phosphates or phosphoric acid are mixed, even when the mixture is made with the greatest care and in perfectly definite proportions. Very small variations in the conditions of the process materially affect the results.

7. A large proportion of the salts of this series crystallize only from sirupy solutions, and are consequently difficult to purify by recrystallization.

8. When new salts result from a double decomposition the phospho-tungstate formed does not often correspond in composition to that from which it is derived. It may be of a higher or of a lower order.

Preparation and General Properties.—Scheibler prepared the salts which he has described by boiling neutral or acid sodic tungstates with half their weight of phosphoric acid. I have found it more convenient to employ the following methods. Solutions of neutral sodic tungstate, $WO_4Na_2 + 2$ aq, and of hydro-disodic phosphate, $PO_4Na_2H + 12$ aq, in the proportion of n molecules of the former to m of the latter, are to be boiled together for some time. The solution has a very strong alkaline reaction. It is to be neutralized with nitric or chlorhydric acid, and then contains the sodium salt—usually acid—of one or another acid of the series. As the sodium salts do not as a rule crystallize as well as those of potassium, I have sometimes found it advantageous to add a solution of potassic bromide or nitrate, when, after some hours, crystals of a potassic salt usually separate in abundance, often in fine colorless and transparent crystals. If a large excess of acid is added at once to the mixed solution of sodic tungstate and phosphate, an acid sodium salt is often precipitated immediately, and almost always after standing a day or two. But it must be remarked that in this case the proportion of tungstic and phosphoric oxides is not always that which existed in the original mixture. In some cases I have fused the tungstate and phosphate together in definite proportions in a large platinum crucible, but this method does not present any special advantage. In other cases I have dissolved tungstic oxide in solutions of alkaline phosphates. Finally, I have in a few instances employed the original method of Scheibler. The alkaline phospho-tungstates, when not too highly acid, are usually rather easily soluble in water, but in the act of solution they almost always undergo a certain amount of decomposition, a white crystalline powder being formed which is comparatively insoluble. Sometimes the solution becomes milky at once, and remains so for a very long time. In all cases it must be allowed to stand until it becomes perfectly clear, and then poured upon the filter without disturbing the precipitate, as the filtrate would otherwise be turbid.

The alkaline phospho-tungstates are not decomposed by hydric sulphide except to a very limited extent. A current of the gas usually produces a blue color from the reduction of a small portion of the tungstic teroxide to the lower oxide W_2O_5. When an alkaline sulphide is added to a solution of a phospho-tungstate a similar reduction is produced. The addition of chlorhydric acid then gives only a small precipitate of tungstic sulphide. Zinc readily reduces a portion of the teroxide to the blue oxide, but the reduction even after some time is very far from complete. The relations of acid phospho-tungstates to salts of the various alkaloids have already been pointed out by Scheibler. In almost all cases nearly insoluble more or less distinctly crystalline precipitates are formed. I find that a beautiful heavy white crystalline salt is thrown down when an acid phospho-tungstate, as, for example, the sodium salt $24\ WO_3 . P_2O_5 . 2\ Na_2O . 4\ H_2O$, is mixed with a solution of urea, or even with urine. In this last case the precipitate contains also slightly soluble salts of potassium and ammonium. It is possible that the reaction may be utilized in animal chemistry. The phospho-tungstates also precipitate egg-albumen as a white flocky substance, which may prove to be a definite salt, in which case the high molecular weight of the acid would be of great value in determining the equivalent of the compound. I have made no experiments in this direction, and throw out the suggestion for what it may be worth.

Mercurous nitrate precipitates all the phospho-tungstates almost completely. The yellow precipitate formed becomes more dense and compact by boiling with the supernatant liquid. It is nearly insoluble in pure water, but dissolves to some extent even in very dilute nitric acid. Dilute chlorhydric acid decomposes the salt, phospho-tungstic acid being set free. The mercurous salts of the series are the only ones which are sufficiently insoluble to be available in analysis.

Soluble salts of the different series of phospho-tungstates usually possess a strongly marked bitter taste. In a single instance the taste is at once sweet and astringent. The salts which are acid in constitution exhibit a strongly marked acid reaction.

Analytical Methods.—To determine the sum of the percentages of tungstic and phosphoric oxides the salt was dissolved in water or dilute nitric acid, and the two oxides precipitated together by means of mercurous nitrate with the addition of mercuric oxide, as in the estimation of tungstic oxide in the alkaline tungstates already described. This method gives good results only when used with great care, as my assistant, Dr. Gooch, observed that the high temperature and long-continued heat required to expel the whole of the mercury also drove off phosphoric oxide, so that the results frequently varied very materially, and were almost always too low. I have sometimes preferred to precipitate the two oxides with mercurous nitrate in small excess from the boiling solution—as in the case of the tungstates—and then to evaporate to perfect dryness on a water-bath, continuing the heat until the whole of the free nitric acid was expelled. The dry mass of mercurous phospho-tungstate and basic nitrate adheres somewhat to the evaporating dish, but not so as to render its removal very difficult. Dr. Gooch found that the adhesion was almost entirely prevented by first evaporating the solution and precipitate to a small volume, and then adding water in considerable quantity and evaporating again, this time to perfect dryness. No phosphoric oxide is vaporized on ignition for an hour at a cherry-red heat, and it is not usually necessary to ignite the mixed oxides a second time so as to insure a constant weight, though it is always better to do so. The yellow powder remaining after ignition is a mixture of tungstic oxide, WO_3, and phosphoric oxide, P_2O_5, from which water removes a portion, but not the whole, of the latter. The quantitative determination of the sum of the two oxides by this method is very nearly, but not absolutely accurate. A trace of phosphoric acid almost always remains in the filtrate from the mercurous salt, and may be detected by evaporating this to dryness, expelling the mercurous oxide by heat, and then igniting a portion of the residue with magnesium wire. The loss of phosphoric oxide is, however, extremely small, and probably never exceeds two or three hundredths of one per cent. The tungstic oxide was always determined by subtracting the phosphoric oxide as directly determined from the sum of the two oxides. My various attempts to determine the two oxides together by precipitation with salts of lead or barium, after neutralization with an alkali, proved failures in all cases.

The precise quantitative separation and estimation of phosphoric oxide in the phospho-tungstates is a matter of no small difficulty. After many trials of various methods, the separation by means of magnesia-mixture was found to give the best results, magnesic chloride being employed. Only, in all cases in which this method is used, it is necessary to redissolve the ammonio-magnesic phosphate first precipitated, and to precipitate the salt a second time with ammonia. The whole subject was specially investigated by Dr. F. A. Gooch, and I shall do him and the process the fullest justice by referring to his paper in Volume I of this Journal. Since the publication of Dr. Gooch's paper, I have also used in many cases the following process, which gives excellent results. The phosphoric oxide is to be precipitated in the usual manner as ammonio-magnesic phosphate, and well washed with magnesia-mixture and ammonia. The precipitate is to be redissolved in chlorhydric acid, ammonia added in small excess, and afterward acetic acid, until the reaction is faintly but distinctly acid. The phosphoric oxide is then to be precipitated from the last solution by uranio-sodic acetate in excess. The precipitate must be allowed to settle completely, and the clear supernatant liquid poured upon the filter without disturbing the precipitate. A moderately strong solution of ammonic nitrate is then to be added, and the precipitate again allowed to settle. After repeating this process two or three times, the precipitate may be brought upon the filter and washed with solution of ammonic nitrate. In this manner there is no danger of obtaining a turbid or milky filtrate. After drying, the precipitate is to be ignited, moistened if necessary with nitric acid, and again ignited. This process is somewhat longer than that by double precipitation and estimation as magnesic pyrophosphate, but is, I think, rather more accurate. In almost all the analyses, by either method, the filtration and washing of the precipitate were effected by means of the asbestos filters devised by Dr. Gooch.* It is hardly possible to speak too highly of this admirable contrivance, which in a very large number of cases is to be preferred to any other mode of filtering, and which has been in daily use in my laboratory for nearly two years, with scarcely a single instance of failure. In many of the earlier analyses the phosphoric oxide was precipitated as ammonio-magnesic phosphate after the addition of citric acid in quantity about equal to the weight of salt taken. Dr. Gooch's later experiments showed that this method gave results which were about 8 per cent. too high when the percipitate—as was always the case—was not redissolved and thrown down a second time. In some cases I have applied this determination as a correction to the direct result of the analysis.

As in the analyses of the alkaline tungstates, I have usually determined the alkali by difference, making direct estimations only in doubtful cases. Ammonia was always expelled by boiling the salt with sodic hydrate, collecting in chlorhydric acid, and weighing as ammonic chloride. Baric oxide was also sometimes estimated by difference. When precipitated from a solution of baric phosphotungstate by sulphuric acid, the sulphate always contains phosphoric oxide, and the same is true when ammonic carbonate and

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*This Journal, Vol. 1, p. 317.

ammonia are employed. Phospho-tungstates which are insoluble in water may be resolved by fusion with an alkaline carbonate, preferably by the mixed carbonates, CO_3KNa. Water is best determined from the loss by ignition, but in some cases I have found it best to ignite with a weighed quantity of borax.

Twenty-four-atom Series. Phospho-tungstic Acid.—The acid is most conveniently prepared by decomposing mercurous phospho-tungstate by dilute chlorhydric acid. I have found it best to proceed as follows. To the mixture of 24 molecules of normal sodic tungstate and 2 molecules of sodic phosphate in solution, after boiling for some time, dilute nitric acid free from chlorine is to be added until the reaction is quite distinctly acid. The solution is then to be precipitated hot by mercurous nitrate in small excess, and the yellow flocky mercurous salt washed thoroughly by decantation with hot water. Toward the end of the operation a few drops of solution of mercurous nitrate may be added to the water, as the washings are otherwise apt to become milky. After washing, dilute chlorhydric acid is to be added in small quantities at a time until the yellow color disappears, and is replaced by the white of mercurous chloride. It is well to set aside a small quantity of the mercurous phospho-tungstate, and to add this to the solution of the acid so as to insure the separation of any remaining traces of chlorhydric acid. After complete subsidence the supernatant liquid is to be filtered off clear and then evaporated *in vacuo* over sulphuric acid. The sirupy faintly violet liquid gives splendid large transparent crystals of phospho-tungstic acid, which are sometimes colorless and sometimes sulphur-yellow. The crystals effloresce with great rapidity, and therefore do not admit of measurement. They appear to be regular octahedra. The solution of the acid is colorless, and has a strongly acid reaction and bitter taste. Of these crystals—

1.2791 gr. lost on ignition	0.1809 gr. water	=14.14 per ct.
1.3005 gr. lost on ignition with fused borax	0.1842 gr. water	=14.16 per ct.
1.4151 gr. gave	1.2130 gr. $WO_3+P_2O_5$	=85.72 per ct.
1.5416 gr. gave	1.3201 gr. $WO_3+P_2O_5$	=85.64 per ct.
1.7365 gr. gave	0.0616 gr. $P_2O_7Mg_2$	=2.26 per ct. P_2O_5

The analyses lead to the formula

$$24\ WO_3 . P_2O_5 . 6\ H_2O+47\ aq, \text{ or } W_{24}P_2O_{71}(HO)_{12}+47\ aq,$$

which requires:—

		Cal'd.	Mean.		
24 WO_3	5568	83.55	83.57	83.53	83.61
P_2O_5	142	2.13	2.11	2.11	
53 H_2O	954	14.32	14.15	14.14	14.16
	6664	100.00	99.83		

As the phosphoric oxide in the analysis was determined after a single precipitation, a correction of 0.15 is applied to the direct result of the analysis. The crystals had slightly effloresced in drying, which explains the deficiency in the water.

A quantity of the 18-atom potassium salt 18 $WO_3 . P_2O_5 . 6 K_2O + 26$ aq was dissolved and precipitated by mercurous nitrate. The mercurous salt was then decomposed by dilute chlorhydric acid, and the solution of phospho-tungstic acid obtained evaporated in a flask at about 50° C. by means of a water air-pump, and then allowed to stand in a partial vacuum over sulphuric acid. After some days splendid colorless crystals formed, which appeared to be octahedra, but which on standing became columnar in structure, opaque and yellow. The analyses of these crystals corresponded very closely to the formula

$$24\ WO_3 . P_2O_5 . 6\ H_2O+34\ aq, \text{ or } W_{24}P_2O_{71}(HO)_{12}+34\ aq,$$

as the following analyses show :—

1.4482 gr. lost on ignition 0.1636 gr. water = 11.30 per ct.
and gave 0.0492 gr. $P_2O_7Mg_2$ = 2.17 per ct. P_2O_5
1.5109 gr. lost on ignition 0.1708 gr. water = 11.31 per ct.
and gave 0.0521 gr. $P_2O_7Mg_2$ = 2.20 per ct. P_2O_5

		Cal'd.		
24 WO_3	5568	86.59	86.50	86.53
P_2O_5	142	2.20	2.20	2.17
40 H_2O	720	11.21	11.30	11.31
	6430	100.00		

The yellow columnar mass, after re-solution and standing over sulphuric acid *in pleno*, gave perfectly colorless regular octahedra, which corresponded to the formula

$$24\ WO_3 . P_2O_5 . 6\ H_2O+55\ aq, \text{ or } W_{24}P_2O_{71}(HO)_{12}+55\ aq.$$

		Cal'd.		
24 WO_3	5568	81.78	81.75	81.76
P_2O_5	142	2.08	2.14	2.15
61 H_2O	1098	16.14	16.11	16.09
	6808	100.00		

In the cases of the two last-mentioned hydrates of the acid, the phosphoric oxide was determined by two successive precipitations as ammonio-magnesic phosphate. The analyses leave no doubt as to the constitution of the acid. Scheibler obtained two different phospho-tungstic acids, to which he gave respectively the provisional formulas

$$H_{15}PW_{11}O_{43}+18\ H_2O,\ \text{and}\ H_{11}PW_{10}O_{38}+8\ H_2O.$$

I should double these and write

$$22\ WO_3 . P_2O_5 . 6\ H_2O+45\ \text{aq, or}\ W_{22}P_2O_{65}(HO)_{12}+45\ \text{aq.}$$
$$20\ WO_3 . P_2O_5 . 6\ H_2O+21\ \text{aq, or}\ W_{20}P_2O_{59}(HO)_{12}+21\ \text{aq.}$$

I have not obtained the acid of the 20-atom series, though I shall show further on that there is at least one well-defined salt in which the ratio of tungstic to phosphoric oxide is as 20 to 1. Scheibler does not give the method which he employed for the separation of the two oxides, and I consider it at least probable that his acid

$$22\ WO_3 . P_2O_5 . 6\ H_2O+45\ \text{aq}$$

is identical with the first of the three hydrates which I have described above.

The solution of phospho-tungstic acid forms a colorless heavy oily liquid, with a high refracting power. It has an acid as well as bitter taste, and readily expels carbonic dioxide from carbonates. On standing for some days, the solution undergoes partial decomposition with deposition of a white crystalline powder. This powder is also almost always deposited, in greater or less quantity, in the preparation of the acid, but I could not obtain it in a state of purity sufficient for analysis. It may be worth while to note as a possible source of difference, that Scheibler obtained his acids by the decomposition of the corresponding barium salts by dilute sulphuric acid. The method of preparation which I employed is, I think, preferable.

24 : 2 *Acid Sodic Phospho-tungstate.*—When chlorhydric or nitric acid is added in large excess to a solution of normal sodic tungstate, and of hydro-disodic phosphate containing 24 molecules of the former to 2 of the latter, a salt is obtained which is usually colorless when chlorhydric acid is employed, and pale sulphur yellow when nitric acid is used. This salt crystallizes more easily than the other salts of sodium. According to Dr. Gooch, the small granular crystals appear to, be either monoclinic or triclinic. They are readily soluble in water, but invariably undergo a slight decomposition in

the act of solution, a small quantity of a white crystalline powder being formed which is insoluble, or but slightly soluble. The yellow and the colorless crystals have the same crystalline form and the same reactions. Their constitution is also the same, as the following analyses show:—

I.

1.4900 gr. lost on ignition	0.1107 gr. water	= 7.43 per ct.
1.1100 gr. gave	1.0016 gr. $WO_3+P_2O_5$	=90.23 per ct.
1.8072 gr. gave	0.0679 gr. $P_2O_7Mg_2$	= 2.40 per ct. P_2O_5

II.

0.9913 gr. lost on ignition	0.1809 gr. water	= 7.34 per ct.
0.8945 gr. lost on ignition	0.0658 gr. water	= 7.32 per ct.
1.0745 gr. gave	0.9698 gr. $WO_3+P_2O_5$	=90.26 per ct.
1.1508 gr. gave	0.0420 gr. $P_2O_7Mg_2$	= 2.33 per ct. P_2O_5

III.

1.4933 gr. lost on ignition	0.1115 gr. water	= 7.47 per ct.
1.3273 gr. gave	1.1969 gr. $WO_3+P_2O_5$	=90.18 per ct.
1.5424 gr. gave	1.3920 gr. $WO_3+P_2O_5$	=90.25 per ct.
1.2990 gr. gave	0.0470 gr. $P_2O_7Mg_2$	= 2.31 per ct. P_2O_5
1.1503 gr. gave	0.0428 gr. "	= 2.38 per ct. "

IV.

1.8027 gr. lost on ignition	0.1349 gr. water	= 7.48 per ct.
1.1559 gr. lost on ignition	0.0860 gr. water	= 7.44 per ct.
1.1269 gr. gave	1.0151 gr. $WO_3+P_2O_5$	=90.08 per ct.
0.9624 gr. gave	0.0367 gr. $P_2O_7Mg_2$	= 2.44 per ct. P_2O_5
0.6787 gr. gave	0.0263 gr. "	= 2.48 per ct. "

Analyses I and II were made with two different preparations of the colorless crystals; III and IV were made with the sulphur-yellow salt. The determinations of ($WO_3+P_2O_5$) in I, II and III were made by the evaporation process without the use of mercuric oxide, but in IV the oxide was employed. As a check upon the quantity of sodic oxide two direct determinations were made in III, the oxide being weighed as nitrate. In this manner—

1.3273 gr. gave 0.0875 gr. NO_3Na=2.40 per cent.
1.2593 gr. gave 0.0924 gr. " =2.68 per cent. Na_2O.

The mean of these two is 2.54 per cent. As the phosphoric oxide in the analyses above cited was determined from a single precipitation as ammonio-magnesian phosphate, I have, as usual in such cases, applied a correction of 0.15 per cent. to the mean. These analyses lead to the formula

$$24\ WO_3\,.\,P_2O_5\,.\,2\ Na_2O\,.\,4\ H_2O+23\ aq.$$

or,

$$W_{24}P_2O_{71}(NaO)_4(HO)_8+23\ aq.$$

		Calc'd.	Mean.						
24 WO_3	5568	88.10	88.04	87.98	88.08	88.02	88.02		88.09
P_2O_5	142	2.25	2.24	2.25	2.18	2.16	2.13	2.29	2.33
2 Na_2O	124	1.97	2.27	....	....	....	....	....	....
27 H_2O	486	7.68	7.49	7.43	7.32 7.34	7.47	7.50	7.48	7.44
	6320	100.00							

The mean of the five determinations of ($WO_3 + P_2O_5$) is 90.20. The formula requires 90.35. There can, I think, be no reasonable doubt as to the constitution of the acid sodium salt, though it is difficult to obtain it in a state of absolute purity. The salt is very conveniently prepared, however, and makes an excellent reagent for alkaloids. For this special purpose it is best to mix the normal tungstate and hydro-disodic phosphate in the proportion of 24 atoms of the former to 3 or 4 of the latter, boil the mixed solutions for a short time, filter, and add chlorhydric acid in excess, but in small successive portions. A precipitate is usually formed on each addition of acid which disappears on stirring the liquid. On standing, a mass of crystals of the acid salt separates. This should be drained, washed with a little cold water, then dissolved in cold water for a reagent, the clear liquid only being used.

The 24 : 2 acid phospho-tungstate of sodium appears to be always formed when an excess of chlorhydric or nitric acid is added to a solution containing sodic tungstate and phosphate, in which the proportion of the latter to that of the former is as 1 to 12, or as 1 to any number less than 12. In other words, it appears to be the limiting term of all the series. When the salt is fused with sodic carbonate, carbonic dioxide is given off, but not in the proportion which might be expected. In one experiment,

2.2298 gr. lost 0.5408 gr. CO_2 and H_2O = 16.94 per ct.
1.2621 gr. lost on simple ignition 0.0922 gr. H_2O = 7.31 per ct.

The ratio of the WO_3 in the salt to the CO_2 expelled is here as 38 : 22, or very nearly as 24 : 13. If the ratio were as 24 : 13, the reaction would be represented by the equation

$$24\ WO_3 . P_2O_5 . 2\ Na_2O + 13\ CO_3Na_2 = 12\ (2\ WO_3 . Na_2O) + P_2O_5 . 3\ Na_2O.$$

A small proportion of neutral tungstate, WO_4Na_2, is probably formed by the further action of the acid tungstate on the alkaline carbonate.

The 24 : 2 acid sodium salt gives no precipitate with the sulphates of zinc, manganese and copper: a white crystalline precipitate with argentic nitrate, and after a short time with baric chloride and ammonic nitrate; no precipitates with calcic and strontic chlorides, but after a short time scanty crystalline salts.

The 24 : 2 acid salt is the only sodium compound of the 24-atom series which I have been able to prepare. When a solution of this salt is carefully neutralized with sodic carbonate, the 6-atom or fully saturated salt, $24\ WO_3 . P_2O_5 . 6\ Na_2O$, possibly exists in the solution, but a definite salt could not be obtained by evaporation. When neutral sodic tungstate and hydro-disodic phosphate are mixed in the proportion of 24 : 2, and acetic acid is added to the solution after boiling for some time, no precipitate is formed, but alcohol throws down a colorless oil which soon solidifies to a white gummy mass. I did not obtain a crystalline well-defined salt from this by re-solution and evaporation, but others may perhaps be more successful.

When a sufficient quantity of sodic carbonate is added to a solution of the acid sodic phospho-tungstate, a mixture of sodic tungstate and sodic phosphate appears to be formed.

$$24\ WO_3 . P_2O_5 . 2\ Na_2O + 25\ CO_3Na_2 = 24\ (WO_3 . Na_2O) + P_2O_5 . 3\ Na_2O.$$

The phospho-tungstate is formed again on adding an excess of acid.

24 : 3 *Acid Potassium Salt.*—When a solution of the 24 : 2 acid sodic salt is added to one of a salt of potassium, a heavy white crystalline, very slightly soluble precipitate is formed, either immediately or after a short time. The salt forms very small granular crystals. It requires a large quantity of water for solution, a white, much more insoluble salt being formed in small quantity by the action of water, so that the liquid is, and for a long time remains, milky. It is best, therefore, simply to wash the precipitate with cold water until this begins to give a turbid filtrate, and then to dry the salt by pressure with woolen paper. The salt is also formed when chlorhydric or nitric acid is added to a solution of potassic phosphate and tungstate in the proportion of 2 molecules of the former to 24 molecules of the latter—the two solutions being previously boiled together for some time in a platinum vessel. The reaction in this latter case may be expressed by the equation

$$24\ WO_4K_2 + 2\ PO_4KH_2 + 44\ HCl = 24\ WO_3 . P_2O_5 . 3\ K_2O + 44\ KCl + 24\ aq,$$

and in the case of precipitation by the acid sodium salt, by the equation

$$24\ WO_3 . P_2O_5 . 2\ Na_2O . 4\ H_2O + 6\ KNO_3 = 24\ WO_3 . P_2O_5 . 3\ K_2O . 3\ H_2O + 4\ NaNO_3 + 2\ NO_3H + 3\ H_2O.$$

In this salt—

1.1478 gr. gave	1.0588 gr. $WO_3 + P_2O_5$	= 92.25 per ct.
1.1764 gr. "	0.0468 gr. $P_2O_7Mg_2$	= 2.54 per ct. P_2O_5
1.7383 gr. lost on ignition	0.0576 gr. water	= 3.31 per ct.
1.7638 gr. " "	0.0578 gr. "	= 3.28 per ct.

The analyses lead to the formula

$$24\ WO_3 . P_2O_5 . 3\ K_2O . 3\ H_2O + 8\ aq.$$

		Calc'd.	Mean.		
24 WO_3	5568	89.93	89.86	89.86	
P_2O_5	142	2.29	2.39	2.39 corrected.	
3 K_2O	283	4.57	4.45	....	
11 H_2O	198	3.19	3.30	3.28	3.31
	6191	100.00	100.00		

In another preparation of the same salt,

0.7340 gr. gave	0.6660 gr. $WO_3 + P_2O_5$	= 90.74 per ct.
1.1400 gr. "	1.0317 gr. "	= 90.50 per ct.
0.8028 gr. "	0.0310 gr. $P_2O_7Mg_2$	= 2.47 per ct. P_2O_5
1.5568 gr. lost on ignition	0.0805 gr. water	= 5.17 per ct.
0.8822 gr. " "	0.0455 gr. "	= 5.16 per ct.

The analyses correspond to the formula

$$24\ WO_3 . P_2O_5 . 3\ K_2O . 3\ H_2O + 14\ aq.$$

		Calc'd.	Mean.			
24 WO_3	5568	88.38	88.30	88.42		88.18
P_2O_5	142	2.26	2.32		2.32	
3 K_2O	283	4.49	4.21	. . .		. . .
17 H_2O	306	4.87	5.17	5.16		5.17
	6299	100.00	100.00			

24 : 3 *Acid Ammonium Salt.*—When a solution of a salt of ammonium is mixed with one of sodic tungstate and phosphate, no precipitate is formed, even after standing; but if a large excess of chlorhydric or nitric acid is poured in, a white or very pale yellowish heavy crystalline salt is thrown down in large quantity. This salt is an acid phospho-tungstate of ammonia, the constitution of which varies with the proportions of the salts employed in its preparation and with the conditions of the experiment.

The different salts, however, resemble each other very closely, and may be described in the same terms. They are either perfectly white or have in mass a faint tinge of yellow and an extremely fine-grained crystalline structure. They are very slightly soluble even in hot water, and give milky emulsions which settle very slowly. Like many other phospho-tungstates and tungstates, they are difficult to wash, as they pass through the closest filter-paper with extraordinary facility. This difficulty may, however, be overcome by adding ammonic nitrate to the wash-water. The acid phospho-tungstates of ammonium are soluble in ammonia-water, but the crystals obtained from such solutions are either ammonic tungstates or salts of series different from that to which the salt dissolved belonged. They are readily decomposed by a red heat, leaving a mixture of tungstic and phosphoric oxides When boiled with mercurous nitrate, they yield mercurous salts and ammonic nitrate.

In one preparation in which sodic tungstate and phosphate were mixed in the proportion of 20 atoms of the former to 2 of the latter, ammonic nitrate was added, and afterward nitric acid. The precipitate was washed with solution of ammonic nitrate, and afterward with alcohol and water, and dried by pressure with woolen paper. Of this salt,

1.3460 gr. lost on ignition 0.1405 gr. $H_2O+NH_3=10.44$ per ct.
1.6407 gr. lost on ignition 0.1707 gr. $H_2O+NH_3=10.40$ per ct.
1.2038 gr. gave 0.0430 gr. $P_2O_7Mg_2=2.27$ per ct. P_2O_5 (twice precip.)
1.3960 gr. gave 0.0504 gr. $P_2O_7Mg_2=2.31$ per ct. " "
1.4890 gr. gave 0.0720 gr. $NH_4Cl =2.35$ per ct. $(NH_4)_2O$.

These analyses lead to the formula

$$24\ WO_3\ .\ P_2O_5\ .\ 3\ (NH_4)_2O\ .\ 3\ H_2O+26\ aq.$$

		Cal'd.	Mean.			
24 WO_3	5568	87.17	87.29	87.27		87.31
P_2O_5	142	2.22	2.29	2.27		2.31
3 $(NH_4)_2O$	156	2.44	2.35		2.35	
29 H_2O	522	8.17	8.07	8.05		8.09
	6388	100.00	100.00			

It will be observed that in this case the 24-atom salt was obtained under conditions which *a priori* should have yielded a 20-atom salt. I have already stated that salts of urea are precipitated from their solutions by acid sodic phospho-tungstate $24\ WO_3\ .\ P_2O_5\ .\ 2\ Na_2O\ .\ 4\ H_2O$. The precipitation is, however, not complete, and the process does not appear to be available as a method of analysis.

When phosphate of aniline and 10 : 4 sodic tungstate are dissolved together, and the solution is boiled for a short time, chlorhydric acid gives an abundant yellowish-white precipitate. On re-solution the precipitate yields pale sulphur-yellow crystals, which are readily soluble in alcohol. Phosphate of para-toluidine behaves in a similar manner; the phospho-tungstate formed is readily soluble, and crystallizes in long yellow silky needles.

I did not succeed in making the insolubility of the acid ammonic phospho-tungstate available in analysis, either for the determination of ammonia or for that of phosphoric acid. For the last-named estimation the phospho-molybdates appear to be far better adapted.

24 : 3 *Acid Barium Salt.*—When 10 : 4 sodic tungstate is dissolved and a small quantity of phosphoric acid is added, the hot solution gives with baric chloride a heavy white flocky precipitate, which readily dissolves in hot dilute chlorhydric acid. The solution, after filtration from a small quantity of flocky matter, is pale yellow, and after some time deposits splendid nearly colorless crystals, which appear to be octahedra. These are readily soluble in hot water without decomposition, and may be repeatedly crystallized without difficulty. Of these crystals,

0.7672 gr. gave 0.6278 gr. $WO_3+P_2O_5$=81.83 per ct.
1.5557 gr. lost on ignition 0.1872 gr. water =12.03 per ct.
1.3732 gr. lost on ignition 0.1641 gr. water =11.95 per ct.
1.6196 gr. gave 0.1547 gr. SO_4Ba = 6.27 per ct. BaO
and 0.0581 gr. $P_2O_7Mg_2$ = 2.29 per ct. P_2O_5
1.2094 gr. gave 0.1158 gr SO_4Ba = 6.28 per ct. BaO

The analyses agree fairly well with the formula

$$24\ WO_3\ .\ P_2O_5\ .\ 3\ BaO\ .\ 3\ H_2O+43\ aq,$$

or,

$$W_{24}P_2O_{71}(BaO_2)_3(HO)_6+43\ aq.$$

The same salt is formed when two atoms of 12 : 5 sodic tungstate are boiled for a time with two atoms of sodic phosphate and chlorhydric acid is added in excess. Baric chloride then gives after a time crystals exactly similar to those described above. In a salt prepared in this manner,

1.0020 gr. gave 0.8173 gr. $WO_3+P_2O_5$ =81.56 per ct.
1.4718 gr. gave 0.1648 gr. SO_4Ba = 6.97 per ct. BaO
and 0.0518 gr. $P_2O_7Mg_2$ = 2.25 per ct. P_2O_5
1.4841 gr. lost on ignition 0.1717 gr. water =11.57 per ct.

		Calc'd.	Mean.			
24 WO_3	5568	79.57	79.57	79.69		79.46
P_2O_5	142	2.03	2.12	2.14		2.10
3 BaO	459	6.56	6.62	6.27	6.28	6.97
46 H_2O	828	11.84	11.78	12.03	11.95	11.57
	6977	100.00	100.09			

The phosphoric oxide determinations are corrected in both analyses. The percentage of baric oxide as determined by difference, which is the more accurate method, is 6.53. The salt effloresces with extraordinary rapidity, so that it is very difficult to dry it for analysis by pressure between folds of woolen paper.

Twenty-two-atom Series.—The phospho-tungstates containing 22 atoms of tungstic oxide to 1 of phosphoric oxide are represented by apparently well-defined salts of potassium, sodium and ammonium. I have not succeeded in preparing the corresponding acid. As already stated, Scheibler has given provisionally the formula

$$H_{15}PW_{11}O_{43}+18\ H_2O,\ \text{or}\ 22\ WO_3\ .\ P_2O_5\ .\ 6\ H_2O+45\ \text{aq},$$

to an acid which he obtained by the decomposition of a salt of barium, and it may be that this is really the acid of the 22-atom series. Further investigations must decide the point. The salts of the 22-atom series closely resemble those of the 24-atom series already described, and are only to be distinguished from them by analysis.

22 : 2 *Potassium Salt.*—The 18-atom potassium salt,

$$18\ WO_3\ .\ P_2O_5\ .\ 6\ K_2O + 30\ \text{aq},$$

gives with chlorhydric or nitric acid a heavy white fine granular precipitate of an acid salt which belongs to the 22-atom series, and which has the formula

$$22\ WO_3\ .\ P_2O_5\ .\ 2\ K_2O\ .\ 4\ H_2O + 2\ \text{aq},$$

as the following analyses show :

1.5679 gr. lost on ignition 0.0318 gr. water = 2.03 per ct.
1.0728 gr. lost on ignition 0.0222 gr. water = 2.07 per ct.
1.5061 gr. gave 1.4250 gr. $WO_3 + P_2O_5$ = 94.61 per ct.
1.1873 gr. gave 1.1253 gr. $WO_3 + P_2O_5$ = 94.78 per ct.
2.1607 gr. gave 0.0927 gr. $P_2O_7Mg_2$ = 2.74 per ct. P_2O_5
2.2367 gr. gave 0.0950 gr. $P_2O_7Mg_2$ = 2.72 per ct. "

		Calc'd.	Mean.		
22 WO_3	5104	92.08	92.11	92.20	92.03
P_2O_5	142	2.56	2.58	2.59	2.57 corrected.
2 K_2O	189	3.41	3.26	....	....
6 H_2O	108	1.95	2.05	2.03	2.07
	5543	100.00			

The salt is very slightly soluble in water. The solution becomes milky, and remains so for a long time. Its formation from the normal 18-atom salt may perhaps be expressed by the equation,

$$10\ (18\ WO_3\ .\ P_2O_5\ .\ 6\ K_2O) + 84\ HCl + 36\ H_2O = 9\ (22\ WO_3\ .\ P_2O_5\ .\ 2\ K_2O\ .\ 4\ H_2O) + 2\ (P_2O_5\ .\ 3\ K_2O) + 84\ KCl + 42\ H_2O.$$

22 : 3 *Ammonium Salt.*—An acid ammonium salt of this series was obtained from a mixture of sodic tungstate and phosphate, to which ammonic nitrate and excess of chlorhydric acid had been added exactly as in the preparation of the 24-atom salt already described. The salt was in very small colorless granular crystals, slightly soluble in cold water, but dissolving to some extent in hot water, giving a milky liquid, settling very slowly. Its other properties are not distinguishable from those of the 24-atom salt. Of this salt,

Gr.		Gr.		Per ct.	Per ct.
0.8697	lost on ignition	0.0805	water and ammonia	= 9.26	= 90.73 $WO_3 + P_2O_5$
1.5911		0.1470		= 9.24	= 90.76 "
0.9086		0.0837		= 9.21	= 90.79 "
1.0934		0.1009		= 9.21	= 90.79 "
1.0934 gave		0.0439 $P_2O_7Mg_2$		= 2.63 P_2O_5	
1.7970 gave		0.0993 NH_4Cl		= 2.68 $(NH_4)_2O$	

These analyses correspond very closely to the formula,

$$22\ WO_3 . P_2O_5 . 3\ (NH_4)_2O . 3\ H_2O + 18\ aq,$$

which requires:

		Calc'd.	Mean.				
22 WO_3	5104	88.30	88.29	88.25	88.28	88.31	88.31
P_2O_5	142	2.46	2.48	2.48 corr.	....	....	....
3 $(NH_4)_2O$	156	2.69	2.68	2.68	...	....	....
21 H_2O	378	6.55	6.60	6.58	6.56	6.53	6.53
	5780	100.00	100.05				

22 : 2 *Sodium Salt.*—It has already been mentioned that, in the preparation of the acid sodium salt of the 24-atom series, a white very slightly soluble crystalline powder is formed in greater or less quantity. This salt cannot be recrystallized for analysis, and must therefore be washed with cold water to remove traces of the soluble acid salt. Hot water dissolves it in small proportion only, the solution remaining milky for a long time. In one preparation of this salt,

0.8405 gr. gave 0.7962 gr. $WO_3+P_2O_5$ =94.73 per ct.
0.8405 gr. gave 0.0330 gr. $P_2O_7Mg_2$ = 2.51 per ct. (twice precip.) P_2O_5
1.4990 gr. lost on ignition 0.0403 gr. water=2.69 per ct.

These analyses lead to the formula

$$22\ WO_3 . P_2O_5 . 2\ Na_2O . 4\ H_2O + 5\ aq.$$

		Calc'd.	
22 WO_3	5104	92.26	92.22
P_2O_5	142	2.56	2.51
2 Na_2O	124	2.25	2.58
9 H_2O	162	2.93	2.69
	5532	100.00	

22 : 4 *Barium Salt.*—This salt was obtained by mixing neutral sodic tungstate and hydro-disodic phosphate in the proportion of 24 : 2, neutralizing with acetic acid, and adding a solution of baric chloride. Small sharp prismatic crystals formed after a short time, soluble in hot water apparently without any decomposition, and separating again from the solution in colorless needles. Of this salt,

0.6900 gr. gave 0.5494 gr. $WO_3+P_2O_5$ =79.62 per ct.
0.6900 gr. gave 0.0826 gr. $P_2O_{11}U_2$ = 2.34 per ct. P_2O_5
0.6734 gr. gave 0.5372 gr. $WO_3+P_2O_5$ =79.71 per ct.
1.5296 gr. gave 0.2163 gr. SO_4Ba = 9.24 per ct. BaO
0.9682 gr. lost on ignition 0.1076 gr. water=11.12 per ct.
0.7064 gr. lost on ignition 0.0787 gr. water=11.14 per ct.

These analyses lead to the formula

$$22\ WO_3 \,.\, P_2O_5 \,.\, 4\ BaO \,.\, 2\ H_2O + 39\ aq,$$

or,

$$W_{22}P_2O_{65}(BaO_2)_4(HO)_4 + 39\ aq.$$

		Calc'd.	Mean.		
22 WO_3	5104	77.37	77.33	77.37	77.28
P_2O_5	142	2.15	2.34	2.34	
4 BaO	612	9.28	9.24	9.24	
41 H_2O	738	11.19	11.13	11.12	11.14
	6596	100.00	100.04		

The phosphoric oxide was precipitated twice.

(*To be continued.*)

CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE COLLEGE.

No. VI.

ON THE DETECTION AND DETERMINATION OF ARSENIC IN ORGANIC MATTER.

By R. H. Chittenden and H. H. Donaldson.

There have been many different methods devised for the detection and determination of arsenic in organic matter, but few are entirely free from objectionable features, or sufficiently accurate to insure perfect reliance upon results obtained by their use. At the present day the toxicologist is expected to answer questions as to rapidity of absorption and rate of elimination, and is required to follow the track of the poison step by step in its course through the body. He has need of methods which will allow of its detection with certainty even though present in very minute quantity. And when by chemical evidence alone the toxicologist is required to state whether the poison has been introduced into the body long before death, or, in other words, whether it is a case of acute or chronic poisoning, none but the most accurate method will suffice to give the information needed. Recently Gautier,* recognizing the need for physiological purposes of a more trustworthy method for the determination of arsenic in animal tissue, has described a new process which has in it many commendable features, but which requires reagents certainly not always obtainable in a state of purity or free from arsenic, though a smaller number is needed than in the commonly used method of Fresenius and Babo.

That a method which requires ten or twelve different chemicals for its completion in the detection of arsenic is a dangerous one, especially in medico-legal cases, no conscientious worker can deny; and a method which involves the use of hydrogen sulphide for 12 to 24 hours will no doubt be gladly dispensed with by those toxicologists who have vainly spent days in the preparation of pure chemicals for the generation of this gas. The method which we have to propose has been suggested by the use of Gautier's process, and some portions of our method may be considered simply

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* Bulletin de la Société chimique, 24, 250.

as modifications of his, while the method as a whole has to recommend it the following features: extreme accuracy, great delicacy, and the use of but three chemicals: nitric acid, sulphuric acid and zinc.

I.—*Method for the Complete Extraction of Arsenic from Organic Matter.*

Gautier's method of destroying the organic matter is based upon the older methods of Orfila* and Filhol,† consisting of successive oxidations with nitric and sulphuric acids at elevated temperatures. The first part of our process is practically the same, except that we use a much lower temperature.

100 grams of the suspected material, cut into small pieces, are placed in a porcelain casserole of 600 cc. capacity and provided with a stirring rod of stout glass 23 cc. of pure concentrated nitric acid are added, and the dish placed on a small air-bath‡ provided with a thermometer and a single Bunsen burner. The mixture is now heated at 150–160° C., with occasional stirring. At first the tissue takes on a yellowish color, then swells up somewhat, becoming finally quite thick; soon changes again, becoming liquid, and then generally requires heating from 1½ to 2 hours, the temperature sometimes being raised to 180° C.

At this point the mass, being now quite thick again, usually takes on a deeper yellow color or orange shade. When this change of color is noticed the casserole is taken from the bath and 3 cc. of pure concentrated sulphuric acid added and the mixture stirred vigorously. The addition of concentrated sulphuric acid to the viscid residue rich in nitric acid and nitro-compounds naturally gives rise, especially at this temperature, to a considerable commotion: the mass becomes brown, swells up, nitrous fumes are copiously evolved, immediately followed by dense white fumes of suffocating odor, while the residue in the dish is changed either into a dry carbonaceous mass or a black, sticky, tar-like mass. Although the oxidation is so powerful, no deflagration takes place, and the carbonization is effected in this manner without the volatilization of any arsenic. The casserole is again placed on the bath and heated

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* Traité de Toxicologie, 1, 494. Paris, 1852.

† Thesis. Paris, 1848.

‡ For air-bath we use an ordinary flat-bottomed tin basin, 7 inches in diameter, 3 inches deep, with a cover provided with an opening 5 inches in diameter. This bath is set in an iron ring fastened to a stout lamp-stand, while the end of the thermometer passes through a small hole near the edge of the cover a short distance into the bath, so that the temperature can be regulated.

for a few minutes at 180° C., then, while still on the bath, 8 cc. of pure concentrated nitric acid are added drop by drop with continual stirring, the object being, as Gautier says, to destroy more completely the organic matter, and at the same time the nitric acid falling drop by drop on the carbonaceous residue tends to prevent the formation of sulphurous acid and the consequent formation of insoluble arsenious sulphide.

After the addition of the nitric acid the dish is heated at 200° C. for fifteen minutes, and when cold a hard carbonaceous residue is the result, entirely free from nitric acid. In working with different kinds of tissue, slight deviations from the above description will frequently be observed. When much bony matter is present the last residue takes on a somewhat different character, owing to the presence of calcium sulphate, and occasionally when the 3 cc. of sulphuric acid are added the oxidation does not at once take place, but requires a little longer heating on the air-bath. But when such is the case the mixture needs constant watching in order to remove the dish from the bath at the first approach of the oxidation.

The arsenic now exists as arsenic acid, readily soluble in water. The carbonaceous residue is thoroughly extracted with boiling water, and in order to avoid all loss is not previously pulverized, but the casserole in which the oxidation took place is filled with water and heated on the water-bath for several hours. The hard mass soon softens, and by repeated treatment in this manner readily gives up all its arsenic to the aqueous solution; it is, however, better to have the carbonaceous residue in contact with different portions of warm water for about 24 hours to insure the complete extraction of the arsenic.

The reddish brown fluid containing some organic matter and arsenic acid is now evaporated on the water-bath to dryness, care being taken that the entire residue is finally obtained in one casserole. This residue* of organic matter and arsenic is dissolved

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* When the residue left by the evaporation of the water is quite large, it is sometimes better to reoxidize it. This is quickly accomplished by adding a few cubic centimeters of concentrated nitric acid to the contents of the casserole and heating on the air-bath at 150–180° C. until a reddish solution is obtained. Then 3–5 cc. of concentrated sulphuric acid are added and the mixture heated at the above temperature until the nitric acid is completely driven off. The thin black fluid is then carefully mixed with the requisite quantity of No. 2 acid, shortly to be described, and introduced into the Marsh apparatus. Frequently quite a heavy, flocculent precipitate separates from the sulphuric acid solution. This does not interfere, but is poured, together with the fluid, directly into the receiving bulb, which is purposely provided with a delivery tube of large calibre.

in a definite quantity of a dilute sulphuric acid with the aid of gentle heat, and in that form, or, as frequently happens, in the form of a fluid with organic matter in suspension, is introduced into the Marsh apparatus in the manner about to be described and the arsenic weighed in the metallic state.

The following results show the accuracy of the method:—

Quantity of Arsenic introduced.	Wt. of Metallic Arsenic found.	Theoretical Wt. Metallic Arsenic.
100 grams beefsteak with .004 gram As_2O_3	.00300	.00303
" " " .004 "	.00300	.00303
" " " .004 "	.00290	.00303
" " " .003 "	.00219	.00227
" " " .005 "	.00369	.00378
" " " .005 "	.00372	.00378

Thus, from the evidence here afforded, we have a method for the determination of arsenic which is extremely accurate, and, above all other things, a method which requires but three chemicals, none of which are extremely difficult to obtain pure, and this for medico-legal purposes is a desideratum long wished for.

II.—*On the Marsh Apparatus.*

There is no method for the detection of arsenic which promises better results, either qualitatively or quantitatively, for toxical purposes, than the decomposition of arsenuretted hydrogen by heat. Indeed, no other method allows of the accurate detection of such minute quantities as the method of Marsh if properly conducted. In making use of this method as a test for arsenic in the usual manner no particular precautions have been taken to have all of the arsenic deposited in the heated tube, and in the qualitative tests for which this method has hitherto been generally used it is well known that the gas is only partially decomposed, and thus it has come to be the general impression that arsenuretted hydrogen is only partially decomposed by heat. The explanation of many poor results which have been obtained by decomposing arsenuretted hydrogen, formed from a known quantity of arsenious oxide, by heat and weighing the metallic arsenic, is not at all difficult. Otto[*] in describing some experiments on this point states that with 10 milligrams of arsenious oxide he sustained a loss of .8 milligram the tube being heated by two lamps and the length of the experi-

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[*] Anleitung zur Ausmittelung der Gifte, 1875, 122.

ment 1½ hours, while the arsenic was introduced in quantities of 1 milligram; but in those experiments in which the arsenic was introduced more rapidly and the time of the experiment shortened, the results were very much poorer.

Dr. Draper* in describing a new method for the determination of arsenic based on the decomposition of arsenuretted hydrogen by heat, proved experimentally that a rapid current of arsenuretted hydrogen passed through a tube heated at five different points by single Bunsen burners was not entirely decomposed, as was evinced by the presence of five distinct mirrors; but when the evolution of gas was very slow, the arsenic was nearly all stopped by the first burner. Thus the cause of the whole trouble, which is almost entirely a mechanical one, lies in the too rapid and irregular evolution of gas, the too rapid and irregular addition of the arsenical mixture, and insufficient length of heated tube.

Gautier† in his recently described process for determining arsenic by the decomposition of arsenuretted hydrogen, has devised an improved arrangement for controlling the evolution of gas, by slowly introducing the arsenic mixed with a definite quantity of dilute sulphuric acid of known strength, later adding the same quantity of a stronger acid, and lastly a still stronger acid; the increasing strength of acid added counteracting the diluting effect of the reaction, so that the strength of acid remains about the same during the entire process of 2½ to 3 hours in the determination of .005 gram of arsenious oxide. Gautier decomposes the gas by passing it through a tube heated with red coals for a distance of 20-25 centimeters.

In making use of the Marsh apparatus according to Gautier's plan, we have so modified it at the suggestion of Prof. S. W. Johnson that it now appears to combine all the essentials of a perfect apparatus.

The flask, a Bunsen's wash-bottle of 200 cc. capacity, is provided with a small separating funnel of 65 cc. capacity, with glass stop-cock. This is a very material aid to the obtaining of a slow and even evolution of gas, a very important desideratum when all loss is to be avoided; for with only a funnel tube, every time a small portion of fluid is added a sudden rush of gas takes place, with probably a small but still more or less appreciable loss. But the separating funnel filled with the acid mixture can be so arranged

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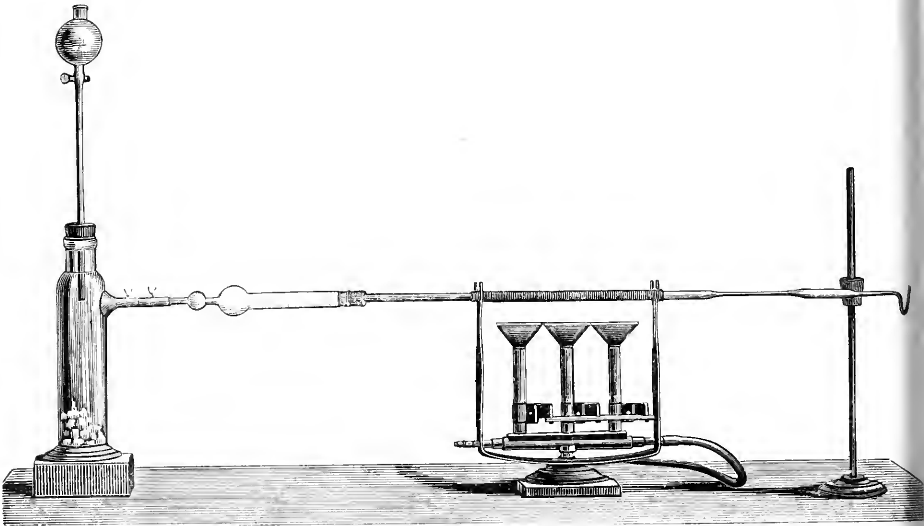
*American Chemist, 2, 456.

† Bulletin de la Société chimique, 24, 258.

as to give a constant and regular supply of fluid at the rate of two or three drops per minute, more or less. The gas generated is dried by passing through a calcium chloride tube, and then passes through a tube of hard glass, heated to a red heat by a miniature furnace of three Bunsen lamps with spread burners, so that a continuous flame of six inches is obtained, and with a proper length of cooled tube not a trace of arsenic passes by. The glass tube where heated is wound with a strip of wire gauze, both ends being supported upon the edges of the lamp frame, so that the tube does not sink down when heated. The small furnace is provided with two appropriate side pieces of sheet metal, so that a steady flame is always obtained. When the quantity of arsenic is very small the tube is naturally so placed that the mirror is deposited in the narrow portion, but when the arsenic is present to the extent of .005 gram the tube should be 6 millimeters in inner diameter, and so arranged that fully two inches of this large tube are between the flame and the narrow portion. When the quantity of arsenic is less the tube can naturally be smaller.



The acids of different strengths, and which for convenience we prepare in considerable quantities, are made as follows:

Acid No. 1.	Acid No. 2.
545 cc. pure conc. H_2SO_4.	109 cc. pure conc. H_2SO_4.
5000 cc. H_2O.	1640 cc. Acid No. 1.

Acid No. 3.	Acid No. 4.
218 cc. pure conc. H_2SO_4.	530 cc. pure conc. H_2SO_4.
1640 cc. Acid No. 1.	1248 cc. H_2O.

25–35 grams of granulated zinc previously alloyed with a small quantity of platinum are placed in the generator, and everything being in position, the apparatus is filled with hydrogen by the use of a small quantity of acid No. 2. After a sufficient time has elapsed the gas is lighted at the jet and the glass tube heated to a bright redness. The arsenical solution in concentrated form is mixed with 45 cc. of acid No. 2, and the mixture passed into the separating funnel, from which it is allowed to flow into the generator at such a rate that the entire fluid is introduced in one hour or one hour and a half; 40 cc. of acid No. 3 are then added and allowed to flow slowly into the generator, and lastly 45 cc. of acid No. 4. The amount of time required will vary with the amount of arsenic: 2–3 milligrams of arsenic will require about two to three hours for the entire decomposition, while 4–5 milligrams will need perhaps three to four hours. Where the amount of arsenic is small only 25 grams of zinc are needed, and but 45 cc. of acid No. 2, 30 cc. of acid No. 3, and 30 cc. of acid No. 4; but when 4–5 milligrams of arsenic are present it is better to take the first mentioned quantities of zinc and acids.

The arsenic being thus collected as a large or small mirror of metal, the tube is cut at a safe distance from the mirror, so that a tube of perhaps 2–6 grams weight is obtained. This is carefully weighed and then the arsenic removed by simple heating; or if the arsenic is to be saved as in a toxical case, dissolved out with strong nitric acid. The tube is then cleaned, dried and again weighed, the difference giving the weight of metallic arsenic, from which by a simple calculation the amount of arsenious oxide can be obtained. The results are exceedingly satisfactory, as is shown by the following, which were obtained by introducing definite quantities of arsenious oxide in the form of a solution mixed with 45 cc. of No. 2 acid, etc.

Quantity of Arsenic introduced.	Wt. of Metallic Arsenic found.	Theoretical Wt. of Metallic Arsenic.
.005 gram As_2O_3	.00373	.00378
.005 " "	.00370	.00378
.004 " "	.00300	.00303
.002 " "	.00151	.00151

In order to ascertain how delicate the detection of arsenic by this form of apparatus is, the following tests were made, using carefully prepared standard solutions of arsenious oxide and accurately graduated burettes.

Quantity of Arsenic introduced.			
.0001	gram	As_2O_3	distinct mirror.
.00001	"	"	" "
.000001	"	"	" "
.0000001	"	"	no mirror visible.

Thus we have the $\frac{1}{1000}$th of one milligram of arsenious oxide as the smallest quantity to be detected by this form of the Marsh apparatus.

Wormley* finds the limit when the amount of fluid is small and the apparatus likewise small, $\frac{1}{50000}$th of one grain of arsenious oxide, which is equal to .000001296 gram of arsenious oxide. That .000001 gram of arsenious oxide is the limit under any circumstances we have proven by taking .0000001 gram and introducing this quantity into a very small apparatus with strong acid, etc., obtaining a negative result.

III.—*Influence of Organic Matter on the Separation of Arsenic as Arsenuretted Hydrogen.*

Dr. T. D. Boeke, of Holland, in a recent paper on the detection of arsenic in organic mixtures,† says, "The admirable method of Marsh in its improved form allows the detection of the minutest trace of arsenic, even in the most complicated mixtures, but with one restriction, viz.: that the solution to be examined be wholly free from organic matter." This statement expresses the prevalent opinion in regard to the influence of organic matter on the Marsh test; but the following experiments, of which those given are but a few of the many tried, show how erroneous such an opinion is. In conducting these experiments with organic matter, after the zinc is placed in the generator, 15 drops of sweet oil are allowed to flow down the side, and this as the fluid is introduced floats on top and thereby prevents any troublesome frothing. The only other thing to be guarded against is the too rapid introduction of the acids whereby loss as well as frothing of the mixture may ensue, and secondly, the heating of the flask by the chemical reaction. If necessary this latter can be prevented by placing the generator in a glass or other dish so that a stream of cold water can continu-

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* Micro-Chemistry of Poisons, 287.

† Chem. News, 41, 177, 1880.

ally play about it, which will keep the flask sufficiently cool to prevent the formation of any hydrogen sulphide which might otherwise show itself in slight quantity.

The first experiments were made with urine.

Quantity of Arsenic introduced.	Wt. of Metallic Arsenic found.	Theoretical Wt. of Metallic Arsenic.
.00475 gram As_2O_3 in 50 cc. urine	.00350	.00359
.00470 " " " "	.00352	.00356
.00001 " " " "	distinct mirror.	
.000001 " " " "	" "	
.00001 " " in 250 cc. urine concentrated to 50 cc.	" "	

Thus it becomes very plain that arsenic contained in urine to the extent of .000001 gram can be detected with certainty, its organic matter not offering any appreciable hindrance.

Mayençon and Bergeret* have devised a new method for the detection of minute traces of arsenic, which they have designed especially for ascertaining the rate of elimination of arsenic by the kidneys. They introduce the urine directly into a flask in which hydrogen is being generated, and ascertain the presence of arsenic by testing the gas as it issues from the end of the tube by means of a paper moistened with mercuric chloride solution; a yellow stain on the paper showing the presence of arsenic The yellow stain is due to the formation of a compound which, according to H. Rose,† contains 1 atom of arsenic, 6 of mercury and 3 of chlorine. By means of this reaction they were able to obtain a yellow color in five minutes by introducing $\frac{1}{10}$th cc. of a fluid containing 5 grams per litre of potassium arsenate. As this amount is equivalent to but .000193 gram of arsenious oxide it cannot be considered extremely delicate, and certainly a method which is dependent entirely on a particular shade of color as an indicator of the presence of the substance looked for is hardly to be compared with such an exact method as that of Marsh. Tests were now made with organic matter in the form of extractive matter from 100 grams of tissue. A large number of oxidations of lean beef in portions of 100 grams made as already described with nitric and sulphuric acids, were extracted with boiling water, and the so obtained aqueous extract evaporated to a thick residue. To each residue from 100 grams of beef definite quantities of arsenious oxide were

* Comptes rend., 79, 118.

† Handbook of Chemistry, 4, 267. Leopold Gmelin.

added in solution, then 45 cc. of acid No. 2, and this mixture introduced into the Marsh apparatus recently described.

The results are as follows:

Quantity of Arsenic introduced.	Wt. of Metallic Arsenic found.	Theoretical Weight of Metallic Arsenic.
.001 gram As_2O_3 in extract from 100 grams beef,	.00070	.00075
.001 " " " " "	.00075	.00075
.002 " " " " "	.00150	.00151
.002 " " " " "	.00150	.00151
.003 " " " " "	.00220	.00227
.003 " " " " "	.00220	.00227
.004 " " " " "	.00290	.00303
.004 " " " " "	.00290	.00303
.005 " " " " "	.00369	.00378
.005 " " " " "	.00369	.00378
.005 " " " " "	.00375	.00378
.005 " " " " "	.00375	.00378
.00001 " " " " "	distinct mirror	
.000001 gram " " " "	faint mirror	

Thus we have abundant evidence that the organic matter which is present here in considerable quantity does not interfere in the least with the recovery of the entire amount of arsenic. Naturally care must be taken that the stronger acid No. 4 does not flow into the generator too rapidly, as it may thereby produce an uncontrollable frothing; the presence of the oil, however, is sufficient to prevent frothing under proper circumstances.

VII.

ESTIMATION OF SULPHUR IN ILLUMINATING GAS BY BURNING IN OXYGEN.

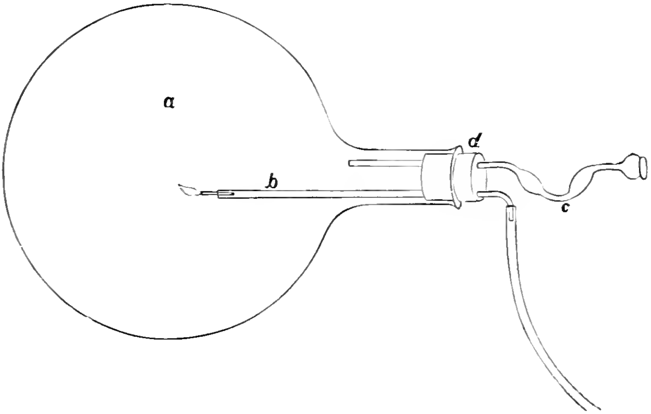
By W. G. Mixter.

The well known method of Letheby and of the Referees and the more recent way of Silliman and Sadtler*, for determining sulphur in gas, are well adapted for finding the average amount during a day, but the apparatus required by any of these methods is not commonly found in laboratories; hence the following method is brought to the attention of chemists who may have to make occasional estimations of sulphur in gas. The method is novel only in

*American Chemist, March, 1877.

the manner of the combustion, for Sauer[*] proposed burning illuminating gas with oxygen in a glass tube and passing the products through a hydrochloric acid solution of bromine. He, however, gave no test results.

The vessel *a* of the figure may be either a 15 litre flask, a large demijohn, or better a carboy. It is filled with oxygen[†] free from sulphur, rinsed with distilled water, loosely corked, and supported on its side over a sink so that a stream of water may be run over it. Or it may be floated in a tub of water and kept cool by pouring water over it. The jet tube *b* is tipped with a roll of platinum foil. The safety tube has at *c* a drop or two of water, which should not resist a water pressure of more than a quarter of an inch. The stopper *d* may be of rubber which has been cleansed with hot potash or a cork. The gas is best measured by a small dry meter which indicates a thousandth of a foot. The gas should flow rapidly through the supply pipes for some time before testing, as well as during the test, so as to get a fair sample of the gas in the mains. When ready for the combustion the gas is lighted at the platinum tip and burned freely till all air is displaced from the meter, then the flame is made quite small, and when the index on the thousandths scale of the meter reaches 0, the jet is introduced into the flask *a*. The meter is then read and the flame is slowly increased. At first a few bubbles of gas



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[*] Fres. Zeit. XII, 32.

[†] Oxygen from potassium chlorate and manganese oxide should stand over water some hours before using.

escape at *c*, and later, air passes in, provided the flask is well cooled. As soon as the gas burns much more dimly than in the air it is turned off, and the apparatus is placed upright and a few drops of bromine are poured in through the tube *c*. The cork and tubes may be removed and the neck of *a* closed with a glass plate. After the cloud which the bromine produces has completely subsided, the flask is rinsed three or four times with just sufficient water to thoroughly wet the sides. The washings are evaporated to small bulk, filtered, and the sulphur is precipitated and weighed as barium sulphate. Ordinary illuminating gas requires about one and a half times its volume of oxygen for its combustion by this method.

Test experiments were made by burning successively 0.3 and 1 cubic foot of coal gas. The duplicate results agreed closely on most days, and a variation of one grain of sulphur in 100 feet of gas was rarely found. But such results are no proof of the accuracy of the method, as illuminating gas is liable to sudden variations in composition; hence the following experiments were made. Weighed quantities of purified carbon disulphide in a sealed bulb were placed in the tube *b*, and a jet of hydrogen was burned in 13 litres of air. During the combustion of the hydrogen the bulb containing the carbon disulphide was broken. The experiments were completed in the way already described. The hydrogen used was purified by long contact with a strong solution of potassium permanganate, and when burned in an air-filled flask gave no reaction for sulphur.

Carbon disulphide taken	0.0772	0.0631 gram
Sulphur found	84.10	84.02
Theory requires	84.21 per cent. of sulphur.	

A Synthesis of Water for a Lecture Experiment.

Hofmann* shows the synthesis of water by burning oxygen and hydrogen in a small platinum retort, and condensing the steam in a cooled spiral. The writer has used for the past two years an apparatus similar in principle, which may be made to yield 1 cc. of water a minute, and which can be put together of cheap and common laboratory apparatus. The figure and directions for making the experiment will make clear the construction of the apparatus. The thin flask *f* is removed and the hydrogen and oxygen turned on and ignited at the end of the compound blowpipe *a*, and the flame is made

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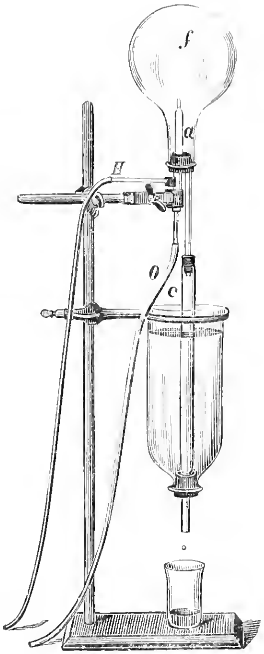
* Berich. d. deutsch. chem. Gesell. 1879, 1122.

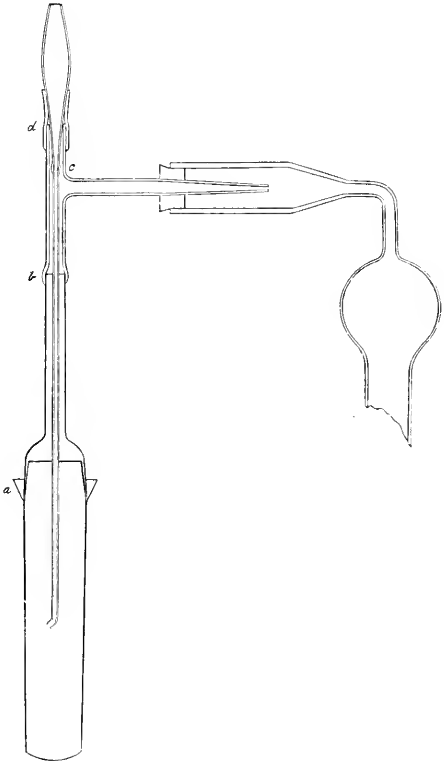


small; the flask *f* is then placed in position, and as soon as the condensed moisture is driven by the heat from the upper half of it the flame is increased. The steam condenses in the cooling tube *c*. When a few drops of water have collected in the beaker, the latter may be held up against the delivery tube, so that the gas passing out shall bubble through the water, and the flow of either gas changed until little or no gas escapes through the water. The volumes of the hydrogen and of the oxygen may now be marked on the gas holders, and at the close of the experiment it will be seen that approximately two volumes of hydrogen and one of oxygen have been consumed. The experiment requires no attention during its progress if the supply of the gases is constant. No precaution is necessary unless the flame is accidentally extinguished, in which case the flask *f* should be filled with air by blowing into it to make sure before putting it over the jet again that it does not contain an explosive hydrogen mixture.

A TUBULATED CRUCIBLE FOR USE IN ESTIMATING VOLATILE PRODUCTS OF IGNITION.

By F. A. Gooch.

In many processes of analysis which involve the collection and direct estimation of volatile products of ignition (such, for example, as the determination of carbon in irons and steels, or of carbon and hydrogen in organic compounds), the use of combustion tubes of glass or porcelain or platinum, either with or without boats of platinum or porcelain as accessories, in connection with proper absorption apparatus, is attended with satisfactory results; but accuracy in processes of this kind which require the application of high temperatures, particularly when the substance under examination is submitted to ignition in contact with a flux or other reagent (as, for instance, in Lipöcz's method of determining the water of constitution of silicates by fusion with sodic carbonate) is not easily secured. It is for use in such processes that the apparatus whose description is appended was devised. Its practical working has been found to be satisfactory, its management easy, and the results of analysis accurate. Its range of applicability to processes, both actual and prospective, whose object is the determination of volatile products of ignition, promises to be extensive.



A platinum crucible shaped, as shown in the figure, in the form of two truncated cones placed base to base, has its upper rim folded twice upon itself so as to present a smooth conical surface on the exterior and an up-turning flange. A conical cap of platinum prolonged upward in a tube fits the outer surface of the crucible near the flange, *a*, in a ground joint. Over the upper end, *b*, of the platinum tube one end of a T tube of lead glass is fused, and the other end of the same branch of the T tube is connected by means of a piece of rubber tubing, *d*, with a glass tube into whose lower end, *c*, is fused a slender platinum tube which extends downward into the crucible and terminates in a slight turn to one side; or, in special cases in which the use of a rubber joint is not permissible, the connection between the inner and outer tubes may be made by fusing the slender platinum tube directly into the upper end of the T tube. The horizontal branch of the T tube is drawn out a little and passes through the stopper of an absorption tube, as shown in the figure. An air-tight joint is made between the cap and the crucible by melting into the flange some easily fusible material like the neutral anhydrous sodic tungstate, or sodic metaphosphate, the former being preferable in most cases; but the seal may be varied, of course, according to the nature of the case in hand.

In using the apparatus the substance to be ignited is put into the crucible, the cap is adjusted, the inner tube set in place and the rubber joint made, the horizontal branch of the T tube connected with the absorption apparatus, the opening in the upper end of the inner tube closed by a cap made of rubber tubing stoppered with a bit of glass rod, and finally the seal melted into the flange with a blowpipe-flame.

As the apparatus now stands it should be air-tight. Next, the cap is removed from the top of the inner tube, and the latter connected with an arrangement for forcing (or drawing) pure air or other gas, according to the purpose of the experiment, through the crucible and absorption tubes, and heat is applied to the crucible. The temperature may be raised until the lower part of the crucible shows a white heat without fusing the seal of sodic tungstate within the flange.

To take the apparatus to pieces after the completion of the operation it is only necessary to disconnect the absorption apparatus, remove the inner tube, remelt the seal and lift the cap. Hot water removes the adhering sodic tungstate very easily.

Some of the dimensions of the particular apparatus which I have in use are as follows:—*

Capacity of crucible	22. cm^3.
Diameter of crucible at top	1.6 cm.
" " " flange	1.9 "
" " " bottom	1.7 "
Height of crucible without cap	9. "
" " tube above cap	5. "
Diameter " " "	0.6 "
Length of inner tube of platinum	13. "
Diameter " " "	0.2 "
Weight of platinum in apparatus	48 grams.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

By C. Loring Jackson.

V.

ON PARAIODBENZYL COMPOUNDS.†

C. F. Mabery.

The preparation of *paraiodbenzylbromide*, $C_6H_4ICH_2Br$, has been described in the first article of this series;‡ but the method there given did not invariably yield good results, the product often being mixed with a black tar which it was very hard to remove completely by crystallization. A more careful study of the conditions of the reaction has shown that this was due to an oily impurity

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* The platinum parts of the apparatus were most skillfully made by Mr. J. Bishop, of Sugartown, Chester Co., Pa. I take this opportunity, too, to call attention, incidentally, to the fact that Mr. Bishop makes a very convenient form of perforated crucible—conical in shape and provided with a cap fitted to the bottom, after a design by Mr. A. A. Blair—intended for use in the process of filtration described by me in this Journal, Vol. 1, page 317.

† Proceedings American Academy of Arts and Sciences. Communicated by the Authors.

‡ This Journal, Vol. I, p. 103.

of the iodtoluol, a very small amount of which was sufficient to destroy a great part or even the whole of the paraiodbenzylbromide: if the paraiodtoluol purified by distillation was carefully pressed between filter-paper, this oil was absorbed, and then the product of the bromiring was nearly white after the first crystallization.

The following substances were obtained from paraiodbenzylbromide by the usual metathetical reactions:

Paraiodbenzylalcohol, $C_6H_4ICH_2OH$, was prepared from the product of the action of sodic acetate on the bromide, by heating it to 160° with aqueous ammonia in a sealed tube: the solid thus obtained was purified by pressing between filter-paper, and crystallization from carbonic disulphide. It was also made* by boiling paraiodbenzylbromide with water for several hours in a flask with a return-condenser. That hydrobromic acid was set free was proved by the acid reaction of the water, and the precipitate of argentic bromide formed on adding argentic nitrate to it, after the organic matter had been removed.

The alcohol prepared according to the first method was analyzed.

0.2508 gr. substance gave 0.3260 gr. CO_2 and 0.0633 gr. H_2O.

	Calculated for C_7H_6IOH.	Found.
Carbon	35.89	35.45
Hydrogen	2.99	2.79

Properties.—It crystallizes from carbonic disulphide or alcohol in small silky white scales; from boiling water, in long needles, with an aromatic odor like that of the corresponding bromine compound, and no action on the eyes; melting-point, 71¾°; very slightly soluble in cold, somewhat more soluble in hot water; freely in alcohol, ether, benzol, and carbonic disulphide.

The *paraiodbenzylacetate* was not obtained pure, because, on account of its instability, a great quantity of substance would have been consumed in its preparation; and it did not seem worth while to sacrifice the large amount of time necessary to prepare so much paraiodbenzylbromide, especially as its decompositions seemed analogous to those of the more accessible parabrombenzylacetate, which will be studied in this laboratory. The following account of the attempts to prepare it is, however, given, as it throws some light upon the nature of the substance. The first difficulty encountered was due to the fact that the sodic acetate only partially decomposed

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* This Journal, Vol. II, p. 88.

paraiodbenzylbromide. The two substances were boiled with absolute alcohol, and an oily product obtained, which solidified at 0°, and after crystallization from alcohol melted at 45°: the results of an analysis of this substance are given under I; it was then heated once more with sodic acetate and absolute alcohol, and the result analyzed, when the numbers given under II were obtained.

I. 0.4007 gr. substance gave 0.4416 gr. CO_2 and 0.0909 gr. H_2O.
II. 0.2936 gr. substance gave 0.3403 gr. CO_2 and 0.0738 gr. H_2O.

	Calculated $C_7H_6IC_2H_3O_2$.	Found.		Calculated C_7H_6IBr.
		I.	II.	
Carbon	39.12	30.05	31.61	28.28
Hydrogen	3.26	2.52	2.79	2.03

These numbers seem to show that the substance was nothing more than a mixture of the acetate and bromide, and this conclusion is strengthened by the fact that it attacked the eyes like the bromide. In order to obtain the acetate from this mixture it would have been necessary to use fractional distillation, which had been found, in the case of parabrombenzylacetate, to cause almost complete decomposition: it was therefore thought better to try to decompose the paraiodbenzylbromide completely by using argentic, instead of sodic, acetate. In this case the product was an oil, which showed no signs of solidification, even after standing in an open watch-glass for some time. The term then came to an end, and it remained exposed to the air during the summer vacation of three months, at the end of which time the watch-glass contained a solid residue, which was proved to be paraiodbenzoic acid by its melting-point and the following analysis of its silver salt:

0.2185 gr. substance gave by precipitation with hydrochloric acid 0.0857 gr. AgCl.

	Calculated for $C_6H_4ICO_2Ag$.	Found.
Silver	30.42	29.62

The formation of this acid under these conditions can be explained by the supposition that the acetate absorbed water from the atmosphere and became converted into the alcohol, which was then oxidized by exposure to the action of the air; and this view is supported by the observation, that a product from the reaction of paraiodbenzyl bromide on sodic acetate dissolved in ordinary alcohol, when precipitated by water, and the oil thus obtained allowed to stand exposed to the air in a watch-glass, deposited crystals, which upon recrystallization melted at 70°, and were, therefore, the alcohol.

It must, however, be remembered that this oil contained some of the bromide, and that the alcohol may have been formed from this instead of the acetate. This conversion of the acetate into the alcohol or acid seemed likely to render its purification so difficult that the experiment with argentic acetate was not repeated. A similar formation of the substituted benzoic acid has been observed in the attempts to purify parabrombenzylacetate.

Paraiodbenzylcyanide, $C_6H_4ICH_2CN$, was obtained by boiling the bromide with alcoholic potassic cyanide, precipitating with water, and crystallizing from alcohol. Its composition was established by the following nitrogen determination:

0.3523 gr. substance gave 17.83 cc. nitrogen, under a pressure of 736 mm. and at the temperature 23°.

	Calculated for C_7H_6ICN.	Found.
Nitrogen	5.76	5.67

Properties.—White plates with a pearly lustre, characteristic odor, and no action on the eyes; melting-point, 50½°; insoluble in water; readily soluble in alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid.

Paraiodalphatoluic acid, $C_6H_4ICH_2COOH$, was obtained by heating the cyanide with fuming hydrochloric acid to 100° in a sealed tube; after four hours, the liquid on cooling became filled with flattened needles, which were purified by crystallization from boiling water. The composition of the acid was fixed by the analysis of its silver salt.

Properties.—Narrow, tapering, white plates, often over two centimeters long, with an agreeable odor resembling that of sweet alyssum; melting-point, 135°; sublimes in branching needles at a somewhat higher temperature; but slightly soluble in cold, readily in hot water, and in alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid. A mixture of potassic dichromate and dilute sulphuric acid oxidizes it, forming paraiodbenzoic acid, which was recognized by its high melting-point. It is freely soluble in aqueous ammonia, but the ammonium salt could not be obtained in the solid state, as evaporation of the solution, whether on the water-bath or *in vacuo*, at ordinary temperatures, decomposed it, leaving the acid, which was recognized by its sparing solubility in cold water and its melting-point of 135°.

Argentic paraiodalphatoluate, $C_6H_4ICH_2COOAg$, was made by adding the solution of the acid in ammonia water, from which the excess of ammonia had been driven off by warming on the water-bath, to argentic nitrate: the white curdy precipitate was washed, dried *in vacuo*, and analyzed.

0.7065 gr. substance, dissolved in dilute nitric acid and precipitated with hydrochloric acid, gave 0.2701 gr. of argentic chloride.

0.1214 gr. substance gave 0.0475 gr. of argentic chloride.

	Calculated for $C_8H_6IO_2Ag$.	Found.	
		I.	II.
Silver	29.27	28.78	29.45

Properties.—A white curdy precipitate resembling argentic chloride, sparingly soluble in boiling water, from which it crystallizes in lustrous plates; readily soluble in dilute nitric acid. The dry salt is only slightly blackened by heat and light.

Baric paraiodalphatoluate, $Ba(C_6H_4ICH_2COO)_2 . H_2O$, prepared by neutralizing baric hydrate with a hot aqueous solution of the acid, and evaporating to crystallization, gave the following results on analysis:—

0.5400 gr. substance dried *in vacuo* lost, when heated to 100°, 0.0153 gr., and gave 0.1881 gr. $BaSO_4$.

	Calculated $Ba(C_8H_6IO_2)_2 . H_2O$.	Found.
Water	2.66	2.83
Barium	20.23	20.48

It forms microscopic white needles, easily soluble in water.

The *calcium salt*, made by treating calcic carbonate with a concentrated aqueous solution of the acid, was also freely soluble in water, and crystallized in slender branching needles.

The solution of the ammonium salt of the acid obtained by dissolving it in aqueous ammonia, and driving off the excess of ammonia on the water-bath, behaved as follows with various reagents:

With *cupric sulphate*, pale bluish-green flocks, insoluble in water, but soluble in acids.

With *ferric chloride*, pale yellowish-brown flocks, insoluble in water.

With *chromic chloride* or *nickelous nitrate*, a green precipitate.

With *cobaltous nitrate*, a pink precipitate.

With *plumbic acetate*, *mercurous nitrate*, or *aluminic chloride*, a white flocculent precipitate.

With *zincic* and *manganous nitrate*, salts which are sparingly soluble in water and crystalline; the manganese salt is flesh-colored. No precipitate was obtained with salts of *cadmium*, *magnesium*, *strontium*, and the *alkaline metals*. In general, its salts resembled very closely those of the corresponding parabromalphatoluic acid.

Paraiodbenzylsulphocyanate, $C_6H_4ICH_2SCN$, was made by boiling an alcoholic solution of potassic sulphocyanate with paraiodbenzylbromide: the oil obtained by precipitating the product with water solidified upon cooling, and was purified by draining on filter-paper, and crystallization from hot alcohol.

0.3661 gr. substance gave 0.4702 gr. CO_2: the water was lost by breaking the chloride of calcium tube.

0.2159 gr. substance gave, according to Carius, 0.1844 gr. baric sulphate.

	Calculated for C_7H_6ISCN.	Found.
Carbon	34.91	35.02
Sulphur	11.64	11.72

Properties.—It crystallizes from alcohol in long white lustrous plates which are often twinned; it has a slight but disagreeable odor, like that of the benzylsulphocyanate; melting-point, 40¼°; insoluble in water; slightly soluble in cold, more so in hot alcohol, freely in ether, benzol, carbonic disulphide, and glacial acetic acid.

PARAIODBENZYLAMINES.

Alcoholic ammonia removed the bromine from the paraiodbenzylbromide with great ease: in fact, it was only necessary to warm the substances together in a flask to obtain a voluminous white precipitate consisting of the secondary and tertiary amines. If a more dilute solution was used, the tertiary amine alone was deposited; while a mixture of this and the secondary amine fell upon adding water. The liquid decanted from this precipitate was evaporated to dryness, and the residue separated by treatment with water into an insoluble bromide of the secondary and the soluble bromide of the primary amine. The mixture of the secondary and tertiary amines, after thorough washing with water, was treated with hot alcohol, which separated without difficulty the more soluble secondary from the but slightly soluble tertiary amine.

Triparaiodbenzylamine, $(C_6H_4ICH_2)_3N$, was purified by recrystallization from ether, dried *in vacuo*, and analyzed.

I. 0.3609 gr. substance gave 8.08 cc. nitrogen, under a pressure of 745.6 mm. and at the temperature 20°.

II. 0.8461 gr. substance gave 21.08 cc. nitrogen, under 742.8 mm. and at 21°.

	Calculated for $(C_7H_6I)_3N$.	Found.	
		I.	II.
Nitrogen	2.15	2.51	2.76

Properties.—White needles arranged in groups resembling hourglasses, with an agreeable odor; melting-point, 114½°; is turned gray by heating, and the melting-point is then much higher; insoluble in water and cold alcohol; very slightly soluble in boiling alcohol, easily in ether, benzol, and carbonic disulphide. A chloride could not be obtained by treating a solution of the base with hydrochloric acid.

Triparaiodbenzylamine chlorplatinate, $[(C_6H_4ICH_2)_3NH]_2PtCl_6$, appeared as a bulky yellow precipitate, on adding a solution of platinic chloride to the amine dissolved in ether. It was washed with alcohol, dried *in vacuo*, and analyzed:

0.7812 gr. substance gave on ignition 0.0886 gr. platinum.

	Calculated for $[(C_7H_6I)_3NH]_2PtCl_6$.	Found.
Platinum	11.32	11.34

Yellow needles nearly insoluble in water and alcohol.

Diparaiodbenzylamine, $(C_6H_4ICH_2)_2NH$, was purified by repeated recrystallization from hot alcohol, dried *in vacuo*, and analyzed.

0.4050 gr. substance gave 12.33 cc. nitrogen, under a pressure of 763.8 mm. and at the temperature 25.5°.

	Calculated for $(C_7H_6I)_2NH$.	Found.
Nitrogen	3.12	3.40

Properties.—White needles with square ends, having an odor somewhat resembling that of the nitrile; melting-point, 76°; insoluble in water; sparingly soluble in cold, freely in hot alcohol, and in ether, benzol, and disulphide of carbon.

The *chloride of the base*, obtained by adding hydrochloric acid to its alcoholic solution, crystallizes in thick, white plates, with a very high melting-point; nearly insoluble in water, slightly soluble in alcohol and benzol, freely in carbonic disulphide and glacial acetic acid. It was proved to be the chloride, by treating its nitric acid solution with argentic nitrate, when argentic chloride was precipitated.

The *bromide of the base* was formed under certain conditions during the preparation of the amines: it was purified by crystallization from alcohol. Short, thick, pointed, white prisms, with a pearly lustre, and a high melting-point; insoluble in water; somewhat soluble in alcohol, more so in ether, benzol, and carbonic disulphide; sparingly soluble in glacial acetic acid. It was proved to be the bromide of the diamine, by treating it with a solution of sodic hydrate, when a base was set free, melting after recrystallization from boiling alcohol at 76°; while bromine was detected in the sodic hydrate by the usual test with chlorine water and carbonic disulphide.

Diparaiodbenzylamine chlorplatinate, $[(C_6H_4ICH_2)_2NH_2]_2PtCl_6$, was obtained as a yellow precipitate on adding platinic chloride to an alcoholic solution of the base: it was washed with alcohol, dried *in vacuo*, and analyzed.

0.3951 gr. substance gave on ignition 0.0609 gr. platinum.

	Calculated for $[(C_7H_6I)_2NH_2]_2PtCl_6$.	Found.
Platinum	15.07	15.42

Properties.—Pale yellow microscopic crystals, grouped like certain forms of frost, almost insoluble in water and alcohol.

Monoparaiodbenzylamine, $C_6H_4ICH_2NH_2$, was most easily obtained by heating paraiodbenzylbromide to 120° in a sealed tube with alcoholic ammonia. The bromide of the primary amine was dissolved out of the product with water, and after treatment with sodic hydrate the free base was extracted with ether. It is an oil which absorbs carbonic dioxide from the air and passes into the *carbonate*, a white crystalline substance melting at 113°.

The *chloride* formed by dissolving the carbonate in hydrochloric acid, crystallizes in slender white needles, which melt at 240°, and are readily soluble in water or alcohol, sparingly in ether.

Monoparaiodbenzylamine chlorplatinate, $[C_6H_4ICH_2NH_3]_2PtCl_6$, was made from the chloride by addition of chlorplatinic acid, and purified by washing with alcohol. It gave the following result on analysis:

0.3560 gr. of the salt gave 0.0795 gr. of platinum.

	Calculated for $(C_7H_6INH_3)_2PtCl_6$.	Found.
Platinum	22.47	22.34

CHLORO-NITRO-PHENETOL.

By Edward J. Hallock.

Monochlorophenetol was first prepared by Henry* in 1869, by the action of phosphorus pentachloride upon phenetol. Five years later Beilstein and Kurbatow† made both the ortho- and parachloro-phenetols from chlorophenol. The latter was probably identical with Henry's chlorophenetol. A more convenient and economical method of its preparation is by acting upon phenetol with potassic chlorate and hydrochloric acid. Several test tubes containing each 5 cc. of phenetol and two or three grams of pulverized potassic chlorate were placed in the draught hood, and a few drops of acid added to each. When the action, which is very energetic, had somewhat subsided, more acid was added until all the chlorate had been decomposed. On pouring into water the resulting product sinks as a heavy yellow oil beneath the water. On distilling a violent bumping usually takes place when the thermometer reaches 100°. After this the thermometer rises rapidly to 200°, and nearly all of the liquid distills over below 240°, where partial decomposition takes place. The distillate remains liquid at ordinary temperatures.

On treating the chlorophenetol thus obtained with nitric acid (concentrated but not fuming), it is attacked quite energetically and converted into a nitro-compound, which is at first oily, but when washed with water soon solidifies to a mass of light yellow crystals, insoluble in water but readily soluble in alcohol and ether. Analysis showed it to be a mono-chloro-mono-nitrophenetol, $C_6H_3Cl(NO_2)OC_2H_5$. It crystallizes in beautiful white needles, resembling the paranitrophenetol described in a former number of this journal. Its fusing point is 61°, which corresponds with that of the parachloro-orthonitrophenetol obtained by Faust and Saame‡ by a much more troublesome method, viz., heating the silver salt of chloronitrophenol with ethyl iodide. These investigators mention it as possessing an unpleasant odor, which is not the case with that obtained by the above method, which also has the advantage of yielding it almost absolutely pure at first.

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* Ber. d. d. ch. Ges. 2, 711.

† Ber. d. d. ch. Ges. 7, 1395.

‡ Zeitschr. f. chem. [2] V, 1869, 450.

The chlorophenetol obtained by the action of potassic chlorate and hydrochloric acid upon phenetol has a peculiar odor not unlike that of oil of anise.

Several attempts have been made to obtain a nitrosophenetol by means of potassic nitrite, and in other ways, but as yet without success; the phenetol is either unattacked, or a nitrophenetol is formed.

COLUMBIA COLLEGE, NEW YORK, *August* 18, 1880.

REVIEWS AND REPORTS.

BRIEF REVIEW OF THE MOST IMPORTANT CHANGES IN THE INDUSTRIAL APPLICATIONS OF CHEMISTRY WITHIN THE LAST FEW YEARS.

(*Continued from p. 150.*)

MATERIALS AND PROCESSES CONNECTED WITH CLOTHING.

General Chemical Treatment of Textile Materials.—The old fashioned method of washing wool, involving entire waste of the large amount of potassium soaps of fatty acids, fatty alcohols, and their compound ethers, which constitute the grease to be removed, has been improved on, to some extent by extraction of the fatty matter with carbon disulphide or petroleum naphtha, but yet more by the Maumené and Rogelet process for making potash, by regulated leaching of the wool, evaporation of the liquid obtained, and either at once burning off organic matter, or charring in close vessels, with utilization for illuminating purposes of the gaseous products given off.

The practice has become established of freeing wool from burs, bits of straw, or other forms of vegetable fibre, by soaking with dilute sulphuric acid, pressing out surplus liquid, and gradually heating the wool up to about 100° C., the vegetable impurities being thus so attacked that they are readily reduced to dust and mechanically removed. Solution of aluminum chloride has been used for the same purpose, as also gaseous hydrochloric acid, and mixed fabrics of wool and cotton or linen may be broken up and the wool recovered in useful form.

The advantage of using *hard* water, containing lime salts, in reeling raw silk has lately been pointed out, the amount of gelatinous matter removed in solution from the surface of the fibre being thus diminished, and loss of tenacity and of beauty in appearance lessened.

Attention has been prominently drawn of late to the extending habit on the part of too many manufacturers of fraudulently "weighting" textile fabrics with foreign substances, introduced to give apparent density to flimsy products of the loom. Cotton and silk have been the materials chiefly treated by such objectionable methods. The sizing legitimately used upon the warp of cotton goods, to give strength and smoothness of surface to the threads in weaving, consists mainly of flour with the gluten partially altered by fermentation, with soap and fatty matter, and should not much exceed five per cent. of the weight of the finished cloth; but white porcelain clay in large quantity, magnesium chloride to attract and retain moisture, and a little zinc chloride producing the same effect and also acting as an antiseptic to obviate mildew, have been extensively employed of late years, sometimes forming altogether fifty or even sixty-five per cent. of the cloth as sold. It is reported also that magnesium sulphate from Stassfurt kieserite has been largely applied to this use, the cloth being passed through a concentrated solution of the salt and then gradually dried.

Silk goods are also notoriously "weighted" to an enormous extent, chiefly in the course of nominal dyeing, both organic and mineral materials being used, among the latter salts of lead, barium, aluminum, etc., with viscid material, such as shellac dissolved in a watery solution of borax, to produce attachment to the cloth, and hygroscopic substances to attract moisture, often with serious injury to the durability of the real fabric, which is more or less corroded and weakened. Samples are reported in which the foreign substances introduced have amounted to two-thirds of the whole weight.

Bleaching, including the Manufacture of Chloride of Lime.—Compulsory condensation of the hydrochloric acid produced in the alkali manufacture by Leblanc's process has for some years tended to fix, even more than formerly, as a regular concomitant of this industry, the production of bleaching powder.

The most important event in the history of the latter has been the really successful solution of the problem of regenerating the manganese employed in such form as to be used over again. The process first introduced for this purpose by Dunlop, although capable of being worked, has never found general acceptance, while that of Weldon has within ten years come to be very extensively, it may almost be said universally employed, and with highly satisfactory results, the loss of manganese being now reduced in well managed works to one and a half per cent., while the production of bleaching powder has within the same time increased threefold, and its price has been reduced by one-half. The process itself, consisting in precipitation of the still liquor, containing manganous chloride, by an excess of calcium hydrate, and oxidation of the precipitate by air forcibly blown for some time through it and the liquid in which it is suspended, has been gradually improved, so that now the chief product seems to be an acid calcium manganite corresponding nearly to the formula

$$\left.\begin{matrix}\mathrm{Ca}\\ \mathrm{H_2}\end{matrix}\right\}(\mathrm{MnO_3})_2.$$

It still yields, however, large quantities of calcium chloride as a by-product, and a satisfactory mode of utilizing the chlorine thus carried off remains, as has already been noted in this report, an important desideratum. The Deacon process for making chlorine at the expense of the oxygen of the air, avoiding altogether the use of manganese, is still in use to a small extent, but has been found to involve a good deal of difficulty, especially in maintaining in a state of activity the sulphate of copper used as the means of promoting the action of atmospheric oxygen.

The conditions for the production of the best chloride of lime have become better understood, particularly the advantageous use of a considerable excess of lime, and a low temperature during the absorption of the chlorine, and the avoidance of packing the product while in too fresh and moist a state.

In the bleaching process itself there is no capital novelty to record as to the use of chlorine, but it is interesting to note the actual introduction upon an industrial, though still limited, scale of the use of hydrogen dioxide, said to be now applied with special advantage to the treatment of Indian tusseh silk. Potassium or sodium permanganate, followed by a weak acid, was also for some time used as a bleaching agent, but has been practically discarded. Atmospheric oxygen in presence of oil of turpentine has been applied to the bleaching of feathers and some other materials of animal origin. One of the most useful of modern improvements, when properly managed, seems to be the combination of chlorine and air bleaching; linen goods in particular, and some of the higher grades of cotton cloth, being satisfactorily bleached by preliminary removal of most of the color with the aid of chlorine, and completion of the process after the ancient fashion of exposure to sun and air, so as combine the rapidity of the one method with the exemption from injury to the fabric of the other.

Preparation of Dye-stuffs.—In the history of these materials five principal phases are observable. First, in the earliest times, the use of native dyes of organic origin, chiefly derived from the vegetable kingdom. Secondly, since the discovery of America and the early voyages of the fifteenth and sixteenth centuries to the west coast of Africa and to India, the use of exotic dyes, also organic. Thirdly, since the middle part of the last century, the employment of mineral dye-stuffs, such as iron buff, chrome yellow, etc. Fourthly, within the last twenty years the introduction of artificial organic colors in vast number and variety, and lastly, within but about ten years, the successful reproduction of natural organic colors by artificial means.

The changes in regard to the preparation of natural dye-stuffs have not of late been very numerous or important. A marked falling off in the production of madder, and of the various partially purified or concentrated forms in which it comes to market, such as garancine, has been the consequence of the introduction of artificial alizarine. Ammonia, instead of lime, has been applied with advantage to the extraction of indigo in Java, and in India it has been found that by using steep-water heated to 110° F. by steam, instead of water at the natural temperature of 92°–95°, an increase of product may be obtained amounting to as much as 25 per cent., the exhaustion of the plant being so complete that further steeping gives practically no more color. For sundry of the long known vegetable dyes the use of concentrated extracts prepared by exhaustion with water and evaporation to solid or pasty consistence, has to a considerable extent replaced the immediate employment of the crude wood, bark or other vegetable material; the character of these extracts, both as to solubility and tinctorial power, has undergone no small improvement.

Our knowledge of the coloring principles of several important natural dye-stuffs has been advanced, as in reference to hæmatoxyline, bresiline, indigotine and orcine; the synthesis of the latter two has been accomplished, though not yet with industrial results,* and will probably be succeeded ere long by that of the others.

Artificial Coloring Matters.—It is, however, chiefly with artificial dye-stuffs that the industrial, as well as scientific history of the last few years has been chiefly occupied. The whole of this brilliant chapter of the subject is so recent, and has attracted such general attention, that it is not easy to decide what may merit special mention as newest and most interesting.

The preliminary treatment of the coal-tar, which forms the main material with which the maker of artificial organic colors works, has become systematized, and in many of its details improved. Particularly has the management of the later stages of coal-tar distillation become better understood. Agitation of the contents of the still, distillation in a current of indifferent gas, and other modifications of practice have improved the yield of the less volatile products, especially the valuable anthracene, whose purification also is better provided for than formerly. The hydrocarbons of lower boiling points—benzene, toluene, etc.—are obtainable of much greater individual purity than some years ago, and in mixtures of more definite and uniform character adapted to the preparation of particular classes of colors. A satisfactory direction for the employment of much of the heavy coal-tar naphtha remains still to be found. Looking to a supposed probability that the supply of coal-tar may be cut short by the progress of electric illumination, Greiff has lately calculated that about 4,000,000 kilos of crude benzene are needed per annum for the production of aniline colors,

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* It has been very recently reported that Baeyer has succeeded in producing artificial indigo by a commercially practicable process, the starting point of which is benzene.

and 900,000 kilos of pure anthracene for making artificial alizarine, and claims that, even should coal gas altogether cease to be made, coal might nevertheless be profitably distilled (with modification of the process) for its other valuable constituents, especially those just named, and that these (benzene, toluene and anthracene) can also be readily obtained, and in sufficient quantity, from the residues of distillation of petroleum of the Caucasus, raising the question also whether American petroleum residues have been adequately examined in this direction.

In regard to the original so-called aniline colors, one of the most important changes has been the application on the great scale of Coupier's process, or a modification of it, for making aniline red (rosaniline salts) without the use of arsenic. This process, consisting essentially in heating together in the presence of an acid nitrobenzene and commercial aniline oil of high boiling point, rich in toluidine, has been adopted by several of the largest manufacturers. The important researches of E. and O. Fischer, Rosenstiehl, and Dale and Schorlemmer, have proved that under the name rosaniline have been included both isomeric and homologous bases of generally similar character, and Dale and Schorlemmer have shown that of these para-rosaniline, with the formula $C_{19}H_{17}N_3$ (identical with that made from para-toluidine) may be prepared from phenol by converting this into aurine, $C_{19}H_{14}O_3$, and heating the latter with an excess of aqueous ammonia; while if aurine be heated with aniline the final product is tri-phenyl-pararosaniline, thus establishing full connection between phenol and the whole series of aniline colors.

The original aniline violet of Hofmann, obtained by the methylation of pre-formed rosaniline salts, has been to a large extent replaced by the "*violet de Paris*," made by first heating aniline under pressure with methyl chloride, or methylic alcohol and hydrochloric acid, thus obtaining methylated aniline derivatives, and then oxidizing such product by heating it in the air, mixed with sand and a salt of one of the heavy metals, usually cupric nitrate, to facilitate the oxidation process. Monnet, Reverdin and Noelting have lately shown that, of the mono- and di-methyl anilines and various isomeric mono- and di-methyl toluidines obtainable from commercial aniline oil in the first stage of this manufacture, pure di-methyl-aniline is the only one which can be advantageously used in the preparation of the violet, in view of adequate yield, solubility, etc., of the product. The finest phenylated blues are now made by heating together very pure rosaniline (made by Coupier's process), a large excess of pure aniline, and benzoic or stearic acid, preferably the former. Aniline green, "*vert lumière*," is now made by heating methyl salts with methyl-aniline violet, thus dispensing with the costly use of iodine. But methyl green has itself been largely replaced of late by "malachite green," made by the action of benzoyl tri-chloride on di-methyl-aniline; the color so obtained exhibiting superior stability in comparison with the methyl and iodine greens. The soluble aniline blacks—"indulines" and "nigrosines"—have come into use for general dyeing purposes, particularly in some forms specially fit for use upon silk goods. The indulines appear to be phenylated derivatives of violaniline, while in the nigrosines phenyl has been substituted for hydrogen in the phenyl groups of the same base. The sulphonates of both are soluble in water as well as alcohol. Almost pure aniline, it has been found, is necessary for the production of these black dyes of the best quality.

Di-phenylamine has come to be largely made by heating together under pressure aniline and its hydrochlorate, and blue and green dyes of peculiar tints are manufactured from it. The hex-nitro-derivative, "aurantia," is also one of the more recently introduced dyes.

The phenol colors, picric acid, iso-purpurate of potassium, and aurine, have shared in the advantage from increased purity of commercial phenol. It has been lately proposed to make picric acid by slowly adding the sulphacid of phenol to concentrated nitric acid, the reaction proceeding slowly, and without requiring application of heat. The formula of aurine (red coralline) has been established, and the conditions of its production from phenol studied.

The beautiful resorcine derivative, eosine, is of comparatively recent introduction, and has established its claim to be considered a valuable addition to the resources of the dyer. The phthaleins of phenol, resorcine and other phenolic substances have of late been converted into eosine and analogous coloring materials by using, instead of bromine itself, a mixture of a bromide and bromate (or corresponding chlorine or iodine compounds) with acetic acid or some other weak acid; and alkaline hypochlorites have also been employed to thus modify the preparation of aureosine and other colors of the eosine class, whose beauty is unfortunately not equalled by their permanence. Methyl, benzyl, and other alcoholic radicles have also been used to form substitution products of resorcine and the colors derivable from it. The tri-atomic phenol, pyrogallol, has given rise to the dyes "galleine" and "cœruleine."

The naphthalene colors have perhaps not established and extended themselves as largely as some other classes, but the calcium or sodium compound of di-nitro-naphthol ("Martius' yellow") still retains its place among valuable dyes.

It is needless to say that artificial alizarine from anthracene has within ten years replaced to an immense extent the natural madder, and become recognized in the very front rank of artificial coloring materials. There have been important additions of late to our knowledge of the isomeric and closely related coloring substances occurring in artificial alizarine, and new nitro- and amido-derivatives of alizarine, with tinctorial properties, have been obtained, and the isomerism of these bodies in a measure worked out by the researches of Perkin, Rosenstiehl, Schützenberger, Morton and others. Alizarine blue, a derivative of mono-nitro-alizarine, attracted for some time attention as affording the means of producing tints like those from indigo, but it proved instable on exposure to light, and has disappeared from commerce. New red, violet, and blue colors have lately been obtained from mono- and di-amido- and nitro- anthraquinone, of which some may perhaps prove permanently useful.

Beautifully colored derivatives of phenanthrene have not long since been announced.

A large class of tinctorially valuable materials has quite recently been introduced, the so-called azo-colors, produced by the reaction of di-azo-compounds upon phenols, amido-compounds, etc. The comparatively long known and permanent "Bismarck brown" consists principally of tri-amido-azobenzene. The prototype of the many recently introduced colors is "chrysoidine," the hydrochlorate of meta-di-amido-azobenzene, and it has been followed by the production of the "tropaeolines" and numerous other parallel derivatives of phenol, cresol, naphthol, resorcine, pyrogallol, &c., modified in various ways by the presence of hydroxyl, nitryl, amido-, sulphonic, and other groups. These new dyes are chiefly of yellow, orange, and scarlet red tints.

Witt has lately described toluylene blue, violet, and pink, representatives of a new class of colors obtained from diamines by simultaneous oxidation of amido- and methyl groups, and forming in a sense a connecting link between the rosaniline series and that of the azo-colors.

The "Cachou de Laval" of Croissant and Bretonnière, although of undetermined and probably indefinite constitution, is a material of too much practical value to be passed over without notice. Made by heating to 250° or 300° C, in close vessels, various waste forms of vegetable fibre, such as saw-dust, spent dye-woods, rags, paper refuse and the like, with caustic alkali and sulphur, the product is obtainable of various colors, chiefly tints of brown, and is remarkable for the firmness with which it attaches itself to cotton cloth, particularly when fixed with bichromate of potash, while its modifying effect upon the brighter coal-tar dyes is very satisfactory, and its cheapness constitutes an important advantage.

Ingenious attempts have been made by Witt, by Graebe and Liebermann, and others to generalize our knowledge of organic colors, and to determine some definite relation between their composition and tinctorial power, but so far such attempts have had but very limited success.

Mordants.—Among the more recently introduced materials for fixing colors upon cloth may be named silicic acid, obtained by immersion of the cloth in solution of sodium silicate, followed by a dilute acid bath; chromic hydrate from otherwise waste chrome alum; and precipitated sulphur, thrown down by successively passing the cloth through solution of sodium thio-sulphate and hydrochloric acid, useful in fixing aniline green, eosine, etc. In attaching to cotton the aniline colors, extensive use is made of albumen, "lactarine," and tannic acid, the last named with or without the addition of an antimony salt (tartar emetic). Eosine has been to some extent fixed by means of lead acetate, and calcium phosphate has been employed for some of the aniline dyes.

Dyeing.—The modifications of long established practice in the actual processes of dyeing have been chiefly matters of detail growing out of the extensive introduction of the artificial organic colors, as, for example, the "animalization" of vegetable fibre, and the use of alcohol as a solvent in the dye-vat. It has been proposed to modify the process of dyeing logwood black by using chrome alum (with iron alum and cream of tartar) instead of bichromate before immersion in the logwood bath. The hyposulphites (hydro-sulphites of Schützenberger) have been successfully used for the reduction of indigotine to hydrindigotine in the indigo vat.

Calico-Printing.—The two capital changes in this art have been the introduction, on a great scale, and with remarkable brilliancy and variety of effect, of the coal-tar colors, and the use of pigments, largely of mineral origin, such as chromic oxide, ultramarine, etc., attached to the cloth by the aid of albumen, in the so-called "surface printing." The field of application of both these methods includes the use of sundry colors not available in general dyeing on account of the difficulty of attaching them uniformly over large surfaces of cloth. Among the most important colors to which this remark applies, is the insoluble aniline black of Lightfoot. The exact constitution of this valuable color remains still uncertain, but the conditions for its development upon cloth by the oxidizing action of potassium chlorate, aided by the presence of a minute amount of a copper or vanadium salt, upon a salt of aniline, usually the hydrochlorate, have been carefully examined. It has been reported that cerous sulphate has been for some time successfully substituted for a vanadium compound in this process, the resulting color being found, it is said, even faster than that made with vanadium.

Tanning.—Probably no branch of industry of equal importance with this presents less of notable improvement in its modern history. Such improvement as there has been belongs more to the mechanical than the chemical side of the manufacture. Some few new tanning materials of exotic origin have been introduced, but none upon a large scale, save perhaps Chinese and Japanese galls, which from their price rather fall into dyers' than tanners' hands. The manufacture of tanners' extracts, as of hemlock bark, chestnut oak bark, etc., has been improved, and the use of such materials extended. The substitution of comparatively pure forms of some of the solutions used for the many crude materials formerly employed has made some progress—as, for example, sodium sulphide instead of "rhusma" (orpiment and lime), for liming preparatory to removal of hair and epidermis, and a weak solution of ammonium chloride or hydrochloric acid, instead of dog or fowl excrement for "bating" where lime has previously been applied and the surplus requires to be removed. None of the many "rapid processes" of ordinary bark tanning can be considered to give altogether satisfactory results; the saving of time is apparently always attended with deterioration of the quality of the leather, particularly as to its durability in use. It has been claimed of late by Böttinger that to *phlobaphene* is essentially due the action of the common oak bark in tanning. In regard to alum tanning, Knapp and v. Wagner have shown some reasons for supposing that the alum and common salt used do not, as is commonly assumed, decompose each other in aqueous solution; but the evidence seems hardly conclusive, and even should the fact be as stated, it might be reversed in presence of the skin in alum tanning. It has been lately proposed to use a salt of iron, ferric sulphate, as a tanning material instead of alum, and still more recently chrome-tanning has been advocated. A method of dyeing, and at the same time partially tanning, raw hide has been introduced in the United States, resulting in the production of a material something like hard vulcanized rubber, and susceptible of a high polish, available for the tips of boots and shoes, and doubtless for various portions of harness and military accoutrements not requiring flexibility. The solutions in which the properly cleansed hide is immersed contain infusion of logwood, nut-galls, cupric sulphate, vinegar, and a salt of iron.

India-rubber, Gutta-percha, etc.—These materials may be briefly noticed here in relation to the manufacture of water-proof clothing, although their applications are so numerous and varied that it is not easy to assign them any single place in a classification of chemical substances founded on their uses. Great extension of the manufactures based upon these substances has for years been going on, but most of the novelty of such manufactures has had reference to varied and chiefly mechanical details of application, not to general chemical treatment. The supply of crude caoutchouc has been greatly increased by systematic search for it in many countries, and from different botanical sources. The quality of the best soft vulcanized rubber has been sensibly improved, as exhibited in the extremely thin and light water-proof garments made from it. A very important improvement has lately been proposed, but the result not yet fully tested by experience, consisting in the admixture with rubber before the vulcanizing process is applied, of ten per cent. or more of very finely subdivided vegetable fibre, the object being to confer a certain degree of porosity so that the objection to rubber clothing, shoes, etc., from the retention of perspiration may be obviated. Perhaps the most noteworthy direction of improvement in the preparation of vulcanized rubber has been that of the production of hard rubber of the higher grades, such as the imitation of ivory for billiard balls, piano keys, etc., by an intimate mixture of caoutchouc and calcined magnesia, strongly compressed and hard vulcanized.

Although of altogether different chemical character, the most recently introduced and on the whole most important substitute for hard rubber in many of its applications may be mentioned in connection with it, namely, "celluloid," the curious material produced by converting paper into pyroxyline, grinding the product along with camphor so as to secure very intimate mixture, pressing and moderately heating the resultant mass. The extraordinary toughness of this material, giving it a character intermediate between that of vulcanite and horn, the readiness with which its appearance may be modified by coloring matters so as to imitate various natural substances, such as ivory, tortoise-shell, coral, etc., the high polish of which it is susceptible, and its inalterability by water and most other agents likely to be brought in contact with it in common use, have already secured for it extensive employment for a multitude of different purposes.

J. W. MALLET.

(*To be continued.*)

REPORT ON PROGRESS IN PHYSIOLOGICAL CHEMISTRY.

[Continued from p. 212.]

In 1879 E. Salkowski* made the observation that human urine distilled with tartaric acid yielded in the distillate a body which was characterized by a red color when treated with pure nitric acid. Later he has shown that the body does not exist free in urine, but is a product of the action of tartaric acid. Munk has found the same substance in the contents of the small intestines, and Salkowski has found that it is formed from albumin by pancreatic fermentation even in 14 hours, and by the continued digestion of horn substance he has succeeded in isolating considerable of the body, together with indol and phenol. The body thus formed is an acid of slight aromatic odor, and after repeated crystallization from alcohol has much the appearance of benzoic acid; analysis shows it to be phenylacetic acid. Further investigation by E. and H. Salkowski† has shown that by the pancreatic digestion of albumin another aromatic acid is formed. Flesh thoroughly extracted with water and alcohol and then dried was the material used. 125 grams of this tissue with 3 litres of water, 9 grams of sodium carbonate, and the pancreatic gland of a dog, were digested 13 days at 40° C. After the removal of the albumin by boiling, and the higher fatty acids by separation as baryta soaps, fractional distillation was resorted to, whereby butyric and valeric acids were removed. The fraction obtained above 250° C. solidified on cooling to a crystalline mass, which, after purification, furnished .7 gram of white crystals. The acid thus obtained was phenylpropionic or hydrocinnamic. From warm concentrated aqueous solutions it separates as an oil, from dilute solutions as glistening needles melting at 47–48° C., and giving by oxidation benzoic acid.

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* Zeitschr. fur physiolog. Chemie, 2, 420. † Ber. d. d. chem. Gesell. 12, 107.

Phenylpropionic acid was also found in fresh flesh. The relation of phenylacetic acid to indol is a very suggestive one. The formation of indol by the pancreatic digestion of albumin was first suggested by Kühne, but lately both Kühne and Nencki have explained clearly that indol is simply a product of the putrefaction of albumin and not formed by the pancreatic ferment, and it is quite probable that the phenylacetic acid also is simply the product of the putrefaction of albumin, but this does not hinder its formation in the body, for that putrefactive changes take place in the intestinal canal is a well established fact.

Recently Baeyer* has effected the synthesis of oxindol, and he considers it to be simply the inner anhydride of orthoamidophenylacetic acid, this latter body being formed from phenylacetic acid by a simple process. The oxindol formed from phenylacetic acid by Baeyer's process gives, when heated with zinc dust, indol, and in all other respects shows itself to be pure oxindol. So that it appears quite plausible that phenylacetic acid and indol, as regards their formation by pancreatic fermentation, stand in close relationship to each other, which could perhaps be explained by a comparison of the quantitative proportions of each substance at different stages of the putrefaction. It has also been pointed out that phenylpropionic acid may stand in similar relations to skatol.

In order to ascertain if different kinds of albumin would yield these two aromatic acids, E. and H. Salkowski† conducted a number of experiments, both with and without the addition of any pancreatic fluid. Their method was to digest 50 grams of the dry albumin with 1 litre of water containing 15 cc. of a saturated solution of sodium carbonate at 40° C., occasionally adding a few drops of a solution containing *Bacillus subtilis*. After a longer or shorter time (2½-60 days) the mixture was distilled to about one-sixth of its volume and both residue and distillate examined. In this way blood-fibrin and muscle-fibrin yielded constantly from 2½-13 days phenylpropionic acid to an amount never exceeding .5 per cent. of the dry albumin. Serum-albumin after 37 days digestion furnished phenylacetic acid in considerable quantity; traces of the acid were to be found even after 13 days. In the fermentation of flesh succinic acid was found in not inconsiderable quantity at the first stage of the decomposition, being detected even after 20 hours. It was also noticed that both horn substance and serum-albumin differ from flesh in that they do not so readily undergo the fermentation. In all experiments with flesh the ether extract contained considerable quantities of the higher fatty acids, principally palmitic acid, and when the fermentation had not been of too long duration, oleïc acid also, the acids being found to the extent of 3 per cent. of the dried albumin. In these cases the flesh was previously freed from fat by repeated heating with ether. Serum-albumin likewise yielded fatty acids, and these two facts have a significant bearing on the

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* Ber. d. deutsch. chem. Gesell. 12, 582.

† Ibid. 12, 648.

possibility of the formation of fat from albumin by processes taking place normally in the animal body. The principal part of the distillate was composed of indol, skatol and phenol.

Hippuric acid is well known as a characteristic constituent of the urine of herbivorous animals. It is also well known as a constituent, in far smaller quantity, however, of human urine and the urine of carnivorous animals, being found in the latter case even when the animal is completely deprived of vegetable food.

Now since E. and H. Salkowski have found that albuminous substances constantly furnish aromatic acids by pancreatic fermentation, or, in other words, that flesh and fibrin furnish regularly phenylpropionic or hydrocinnamic acid, they have proposed the theory that these aromatic acids formed by the breaking up of albumin in the body become oxidized to benzoic acid, and that in this manner hippuric acid might originate from albuminous substances. They have thus been led to study the behavior of phenylacetic and phenylpropionic acid in the organism[*]

A support for such a theory was found in the discovery by Erdman and Marchand[†] in 1842 that cinnamic acid changed within the organism to hippuric acid, which statement was confirmed by Graebe and Schultzen.[‡]

E. and H. Salkowski find by experiment that their supposition is partially correct. Phenylpropionic acid is changed within the body completely into benzoic acid, and appears as hippuric acid in the urine. Phenylacetic acid, on the other hand, is not oxidized, but forms an acid analogous to hippuric acid, which is properly called phenaceturic acid.

Phenylpropionic acid, $C_6H_4CH_2CH_2COOH$, was given to a dog in food (1.5–2 grams of a soda salt daily) and the urine collected and evaporated. In the alcoholic ether extract hippuric acid alone was found, which, heated with hydrochloric acid, decomposed with formation of benzoic acid; no trace of an homologous acid was found. Thus we have a lucid explanation of the hitherto inexplicable phenomenon of the secretion of hippuric acid by animals fed entirely on flesh; for as the phenylpropionic acid is formed very early by pancreatic fermentation, it is clearly not difficult to accept the view that during life a certain quantity of this acid is formed in the intestinal canal. The hippuric acid of herbivorous animals without doubt originates also in part from albumin in this manner. The fact that a hungry animal which lives simply on its own tissue continues to secrete hippuric acid is another indication, as is also the secretion of indican during the condition of hunger, that in tissue and organs also fermentation processes take place which lead to the splitting off from albumin of aromatic substances.

Phenylacetic acid, $C_6H_5CH_2COOH$, was fed in the same quantities as the phenylpropionic acid to several dogs, and phenaceturic acid was found abundantly in the urine, but hippuric acid never rose

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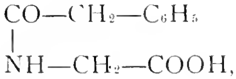
[*] Ber. d. deutsch. chem. Gesell. 12, 653.

[†] Jour. für prakt. Chem. 26, 494.

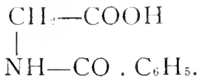
[‡] Annal. Chem. u. Pharm. 142, 346.

above the normal amount. The phenaceturic acid thus formed does not differ in many of its properties from hippuric acid, crystallizing from hot water in thin plates, and when boiled with hydrochloric acid breaking up easily into phenylacetic acid and glycocoll. Its formula is therefore—



$$\begin{array}{l} CO—CH_2—C_6H_5 \\ | \\ NH—CH_2—COOH, \end{array}$$

while hippuric acid is



$$\begin{array}{l} CH_2—COOH \\ | \\ NH—CO\ .\ C_6H_5. \end{array}$$

Several years ago Baumann, while studying the origin of aromatic substances in the body, made experiments which tended to show that under certain conditions phenol is formed during the putrefaction of albumin. The natural supposition was that the phenol is not a direct decomposition-product of albumin, but more probably of the tyrosine formed from albumin. More recently Baumann, in conjunction with Brieger,* has shown that the phenol formed from albumin by putrefactive changes consists in great part of paracresol, and contains only a small proportion of phenol, C_6H_6O. Weyl† has, however, shown that by putrefaction tyrosine can be decomposed with formation of volatile phenol, and at the same time paracresol is formed. Again, Baumann,‡ by experiments on dogs, has shown that the paracresol which appears to a great extent as paracresol-sulphuric acid in the urine, is to a small extent oxidized in the body to paroxybenzoic acid, while the paroxybenzoic acid is decomposed, partially in the body, completely by putrefaction, into phenol and carbonic acid.

In a more recent contribution Baumann§ has attempted to show the relation of these different aromatic bodies as regards their formation, starting with the assumption that they are formed not directly from albumin but from tyrosine. He subjected 6 grams of tyrosine in 5 litres of water to decomposition at 40° C. with a small quantity of pancreas infusion for 2 days. At the end of this time the evaporated fluid yielded no trace of tyrosine crystals, but by proper treatment an acid was obtained which, by recrystallization, showed itself in well formed crystals, and had the properties and composition of hydroparacumaric acid. Thus Baumann arrives at the conclusion that this acid is the first decomposition-product of tyrosine by putrefaction, and that it originates from tyrosine in the same manner as succinic acid from aspartic acid. This decomposition is also of interest as showing something in regard to the constitution of tyrosine. Barth|| had previously shown that tyrosine belongs to the paroxybenzoic acid series, and from his experi-

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* Zeitschrift für physiolog. Chem. 3, 149.

† Ber. d. deutsch. chem. Gesell. 12, 354.

‡ Zeitschrift fur physiolog. Chem. 1, 244.

§ Ber. d. deutsch. chem. Gesell. 12, 1450.

|| Ann. Chem. u. Pharm. 136, 110, also 152, 96.

ment concluded that tyrosine is paroxyphenolamidopropionic acid (amidohydroparacumaric acid).

Thus according to Barth the constitution of tyrosine would be expressed by the following formula:

$$C_6H_4 \left\{ \begin{matrix} OH \\ C_2H_3 \,.\, NH_2COOH, \end{matrix} \right.$$

and this view receives an additional support in the formation of hydroparacumaric acid from tyrosine. The series of phenol-derivatives formed from albumin, or more properly from tyrosine, has been increased by the observations of E. and H. Salkowski,* that by the putrefaction of horn substance and of albuminous matters in general, oxy-aromatic acids are obtained, viz., paroxyphenylacetic acid and paroxyphenylpropionic acid. Thus, according to Baumann, the following series of compounds can be formed from tyrosine by gradual decomposition and oxidation:

$$\underbrace{C_9H_{11}NO_3+H_2}_{\text{Tyrosine}} = \underbrace{C_9H_{10}O_3+NH_3}_{\text{Hydroparacumaric acid}}$$

$$\underbrace{C_9H_{10}O_3}_{\text{Hydroparacumaric acid}} = \underbrace{C_8H_{10}O+CO_2}_{\text{Paraethylphenol}}$$

$$\underbrace{C_8H_{10}O+O_3}_{\text{Paraethylphenol}} = \underbrace{C_8H_8O_3+H_2O}_{\text{Paroxyphenylacetic acid}}$$

$$\underbrace{C_8H_8O_3}_{\text{Paroxyphenylacetic acid}} = \underbrace{C_7H_8O+CO_2}_{\text{Paracresol}}$$

$$\underbrace{C_7H_8O+O_3}_{\text{Paracresol}} = \underbrace{C_7H_6O_3+H_2O}_{\text{Paroxybenzoic acid}}$$

$$\underbrace{C_7H_6O_3}_{\text{Paroxybenzoic acid}} = \underbrace{C_6H_6O+CO_2}_{\text{Phenol}}$$

With the exception of paraethylphenol and paroxybenzoic acid, all of these substances have been detected in the animal body, or by the decomposition of albumin or tyrosine. Paroxybenzoic acid originates in the animal body from paracresol, and it is not found in the urine under normal conditions, according to Baumann's view, simply because the quantity of paracresol is very small. Baumann† is of the opinion that the tyrosine formed in the intestinal canal, as an intermediate product in the decomposition of albumin and readily passing into hydroparacumaric acid, splits up in the body and furnishes the paroxyphenylacetic acid which is

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* Ber. d. deutsch. chem. Gesell. 12, 1438; 13, 189.

† Ibid. 13, 279.

found in the urine, an acid very similar to hydroparacumaric acid. The quantity of this oxy-acid detected in human urine was quite similar in ten different experiments, 25 litres of urine furnishing in each case about ½ gram of the crude acid.

As Weyl* has shown that by putrefaction paracresol is formed both from paroxyphenylacetic acid and tyrosine, it is quite clear that tyrosine must be the mother substance from which the paroxyphenylacetic acid found in the urine originates.

Baumann then observes that if the different bodies placed in the above list are formed successively from one another by putrefaction, paraethylphenol or paroxyphenylacetic acid must be formed from hydroparacumaric acid. In order to ascertain this point the following interesting experiment was conducted on a man, and as preliminary to the actual experiment the following facts were ascertained: The normal daily urine (1260 cc., sp. g. 1.026) did not contain a sufficient amount of the aromatic oxy-acids to permit of their separation in pure condition; further, this quantity of normal urine contained 2.636 grams of sulphuric acid in the form of sulphates, and 0.372 gram of sulphuric acid existing in the form of ethylsulphuric acid. 100 cc. of such normal urine furnished by distillation with hydrochloric acid a distillate which was simply made turbid by bromine water, phenol not being found in weighable quantity. On the following day 5 grams of pure hydroparacumaric acid were dissolved in water and taken at intervals during one hour. The urine of the following 24 hours (1325 cc., sp. g. 1.027) contained 2.207 grams of sulphuric acid in the form of sulphates, and 0.479 gram of sulphuric acid existing as ethylsulphuric acid. 100 cc. of the same urine furnished by distillation with hydrochloric acid a fluid which, with bromine water, quickly gave a crystalline precipitate of a bromine compound of phenol weighing 0.031 gram. From the entire quantity of the urine 0.8 gram of an acid was obtained which, after recrystallization from benzol, was found to be pure hydroparacumaric acid. Thus the greater part of the hydroparacumaric acid given had disappeared in the body, while one part was secreted unaltered, and a still smaller part was decomposed with formation of phenol, which was secreted by the urine as ethylsulphuric acid. Paroxyphenylacetic acid was not formed from the hydroparacumaric acid in a quantity sufficient to be detected.

Baumann then, in discussing the possibility of these different aromatic bodies being formed from each other by alternate oxidation and reduction, suggests that hydroparacumaric acid, under certain conditions, may furnish paroxyphenylacetic acid directly by splitting off of carbonic acid and ammonia, and in support of such a decomposition quotes the behavior of leucine by putrefaction in the presence of air, by which ammonia, carbonic acid and valeric acid are formed.

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* Ber. d. deutsch. chem. Gesell. 12, 354.

R. H. CHITTENDEN.

(*To be continued.*)

THE SUBSECTION OF CHEMISTRY AT BOSTON.

At the Boston meeting of the American Association for the Advancement of Science, the subsection of chemistry was more largely attended then ever before. The prospects are that in another year it will be raised to the dignity of a full section, to be presided over by one of the Vice-Presidents of the Association. At the late meeting Professor J. M. Ordway occupied the chair, and Professor C. E. Munroe was secretary. Next year, in Cincinnati, Professor W. R. Nichols will be chairman, and Professor H. W. Wiley secretary. Prof. G. J. Brush was elected President of the Association.

The Association came together on Wednesday, the 25th of August. On Wednesday and Thursday little real work was done, the first day being devoted to organization and to set addresses, and the second to a visit to Cambridge. Professor Ordway's address as chairman of the subsection was delivered on Wednesday afternoon. It consisted mainly of a brief resumé of late advances in chemistry, especially in some of its applications to the useful arts, and of a plea for the more extended study of the biological side of the science.

On Friday the reading of papers before the subsection began. The first communication was by Professor Wiley, who spoke upon "The rotatory power of glucose and grape sugar." The word "glucose" is applied by the manufacturers to the thick syrup made from corn. The term "grape sugar," on the other hand, is applied to the crystallized product. There are now ten glucose factories running night and day in this country, which consume twenty-one thousand bushels of corn per diem, each bushel yielding on an average twenty-eight pounds of glucose. The yearly yield is therefore 214,620,000 pounds. Five-sixths of this product is "glucose," and one-sixth "grape sugar." The latter is used for mixing with cane sugar by brewers, distillers, vinegar makers, etc. The mixture with cane sugar is sold as "new process sugar." The "glucose" is used also by brewers and distillers, for sizing paper, in making printer's ink rollers, and in enormous quantities for syrup. It is mixed with a few per cent. of cane syrup and sold under a variety of fancy names. Professor Wiley has found that all the commercial glucoses contain notable percentages of dextrine, and upon the latter their rotatory power largely depends. Formulae were given for determining the per cent. of glucose by the polariscope.

Next came one of Professor Leeds' papers on the "Influence of actinism upon iodides."* It was read by D. S. Martin, the author being absent. E. T. Cox followed with an account of some extensive lodes of oxide of antimony in Sonora, Mexico This paper was partly geological in character. The lodes described are from four to twenty feet wide, and exploration to the depth of thirty

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* Published in full by the American Chemical Society.

feet shows that the fissures are filled from wall to wall with the hydrated oxide, almost pure. The ore contains from 60 to 77 per cent. of metal, and the entire deposit probably averages 50 per cent. By going down deeper the oxide may perhaps change to sulphide; but at present there is no evidence of any such alteration. The slight impurity in the ore is silica.

The fourth and fifth papers were by Professor E. W. Morley, who described some tables for use in gas analysis, and recommended a thermometric scale which shows the logarithmic factor for reduction to zero. This is convenient when many analyses are to be made.

The next paper, on "The constitution of the tartrates of antimony," was the joint work of F. W. Clarke and Miss Helena Stallo It will appear in full in this journal, and needs therefore no detailed notice here. It was followed by a communication from Thomas Gaffield, entitled "The action of sunlight on glass." A general classification of the changes of color produced by the sun in nearly colorless glasses, is as follows: 1. From white to yellowish. 2. From greenish to yellowish-green. 3. From brownish-yellow and greenish tints to purple. 4. From light green or greenish white to bluish. 5. From bluish and other tints to darker shades of the same colors. Every specimen of colorless glass exposed for ten years shows some change of color, with the exception of some white flint glass, such as is used for fine glass-ware and optical purposes. The optical glasses studied by Mr. Gaffield, except two pieces of crown glass which became of a yellowish color, showed only very slight changes of tint. Possibly the oxide of lead, which enters largely into the composition of such glass, may act as a protector against changes by sunlight exposure. In experimenting for ten years with colored glasses of the main spectral colors, no change was observed in any pot-metal specimens, save a slight darkening of the purple. A change to a purplish or yellowish color was noticed in the colorless body of some of the flashed and stained specimens, which were originally tinted on the surface only. An experiment with pot-metals, not of the primary colors, but of the hues which most nearly approach those produced in colorless glass by sunlight exposure, showed the following changes: 1. From brownish tints to a flesh-color. 2. From flesh-color to violet or purple. 3. From amber, olive, and purple to darker shades of the same colors. It is interesting to know that, so far as such colors were used in the old cathedral windows, they must have changed in tint; and that the glass which we now see in these old churches and which has suffered sunlight exposure for centuries, is of very different hues from those which it exhibited when it left the artists' studios or the glass factories of mediæval times. A curious fact noticed by Pelouze and by Percy is confirmed by Mr. Gaffield; namely, that with a few exceptions among the colored glasses, all the specimens changed in color by sunlight can be restored to their original tint by the heat of a glass-stainer's kiln. They can again be colored by exposure to sunlight, and this coloration and the decoloration by heat can be carried on indefinitely.

The day's work concluded with two papers by Professor Morley, concerning the ratio of oxygen to nitrogen in air. He presented the following remarkable conclusions. When the air at a given place is cold and the barometer high, there may be a vertical descent of cold air from great altitudes. Samples collected at such times are more likely to approach the composition of the upper atmosphere than those collected at other times. If there be any cause tending to produce an excess of nitrogen in the upper atmosphere, such as, for example, the difference in density between oxygen and nitrogen, then the average per cent. of oxygen in many samples collected at the times above mentioned will be lower than that of other samples. In order to test this supposition, Professor Morley collected samples of air during each time of unusual cold and high barometer from September, 1878, to April, 1879. In 1878 the mean percentage of oxygen in these was 0.16 per cent. lower than in other samples; and in 1879, 0.12 per cent. lower. No source of error could be detected. The inquiry was further pursued by a series of daily duplicate analyses of air during six months, and a comparison of the results with the thrice daily maps of the U. S. Signal Service. He finds a deficiency of oxygen at the times and only at the times when a vertical descent of air at or near the place of collection may reasonably be inferred from the weather maps. The coincidences were plotted by Professor Morley in a series of curves, and are certainly extraordinary.

On Saturday Mr. N. B. Webster spoke "On a solution of ferric gallate and ferric oxalate as a reagent for the quantitative analysis of ammonia." Then C. F. Mabery described some substituted acrylic acids recently investigated by himself with the co-operation of Mrs. R. Lloyd. Diodbromacrylic acid, $C_3I_2BrHO_2$, is made by the action of iodine upon brompropiolic acid. It crystallizes in flat, white, six-sided plates, which are sparingly soluble in cold, readily in hot water; soluble also in ether, benzol, carbon disulphide and ligroin. It readily decomposes carbonates. Melting-point, 160°. Its silver, potassium, calcium and barium salts were prepared and analyzed.

Fuming hydrochloric acid unites readily with brompropiolic acid to form chlorobromacrylic acid, $C_3ClBrH_2O_2$. It forms elongated flat prisms which melt at 70°. In solubility it resembles the acid previously described. Its acid character is very decided, and its silver, potassium, calcium and barium salts were investigated.

Next in order Mr. L. M. Norton discussed the valuation of indigo; after which Professor W. O. Atwater spoke on "The soil supply of nitrogen for plants." The gist of his paper was briefly as follows: Nitrogen is rapidly wasted from the soil, and is the most expensive material to replace in the form of manures. In this country, especially in New England, we have longer and colder winters, with warmer and drier summers, than in Europe. Less of our rain and snow water escapes from the soil in winter with us than abroad, since our ground is frozen longer; while in summer the same is true because of greater evaporation from the surface. Hence in our climate less nitrogen is lost by the soil through leaching than is lost in Europe. Professor Atwater's experiments, carried out in the field by himself and by colleges and private individuals in several States, establish the foregoing conclusions, and show that nitrogen is not so necessary in our soils, and that we can get along with the cheaper mineral fertilizers and less nitrogen than our European competitors.

The next communication was by Professor H. B. Nason, who described some "Incrustations formed in pipes used in gas wells," and exhibited an interesting specimen. Professor W. R. Nichols gave an account of some "Observations on the temperature and chemical character of Mystic Lake, Mass., at different times and at different depths," and Professor C. E. Munroe proposed a "Modification of Berthier's process for the valuation of coal." He substitutes for the crucible used by Berthier an iron tube three feet long and one inch in diameter, open at one end and having a screw plug at the other. The litharge and coal are placed in this tube, which is then heated in a furnace under a steam boiler for about five minutes. The tube, while red-hot, is held vertically in a vise, the plug is withdrawn, and the molten lead is collected in a box lined with plaster of Paris. This process is especially devised for the use of steamship engineers when making purchases of coal.

On Monday but few papers were read before the sub-section. J. L. Kleinschmidt spoke of "Foreign substances in iron"; S. P. Sharples discussed the "Commercial testing of sugar, illustrated by samples of sugar and the instruments used"; and Professor Wiley described the "Influence of heating with dilute acids, and shaking with bone coal, on the rotatory power of glucose." He finds that heating with acids produces a marked effect, diminishing the rotatory power of glucose by one-half. When this fact is not taken into account, a serious error may arise in the estimation of a mixture. The stronger the acid and the longer the heating is continued, the more marked is the effect. Simultaneously with this diminution of rotatory power, the percentage of glucose or of copper-reducing matter may be greatly increased. This shows that intermixed dextrin or other optically active substance is either changed into glucose or has its rotatory power altered. By shaking glucose with animal charcoal, a decided change is effected in its rotatory power, sometimes as much as ten per cent. Thus, in the examination of mixtures, serious errors may arise if bone coal has been used, unless the effect of the latter is taken into consideration.

The closing paper of the day was by Dr. T. Sterry Hunt, "On the genesis of certain iron ores." It is impossible to state Dr. Hunt's conclusions compactly enough for present purposes, and at the same time accurately. He begins with the iron, generally ferrous iron, found in the mineral silicates of crystalline rocks. This, by sub-aerial decay, is liberated as ferric hydrate, which in turn is reduced to ferrous hydrate by organic matter, and dissolved in water either charged with carbonic acid or acids of organic origin. From such solutions it is again deposited as limonite, as siderite, as a silicate, or as pyrites, in all of which conditions iron is found in sedimentary formations. The intervention of soluble sulphates, and their reduction through organic agency to sulphides, determines the formation of pyrites in sediment. The changes of siderite and pyrite under atmospheric influences were considered. The latter, by oxidation, yields sulphate, which by the intervention of water holding carbonates, conjointly with oxygen, is converted into hydrous peroxide. Evidence, both experimental and geological, was cited by Dr. Hunt in support of his conclusions.

On Tuesday, E. G. Love presented a communication on "The illuminating gas of New York city," after which two papers were read by A. A. Breneman. The first of these, upon "New colors for salt-glazed pottery," was accompanied by the exhibition of specimens. A vase was shown upon which a vine in green was painted on the ordinary gray body of the stoneware. The range of obtainable colors is very great, so that this cheap ware may be made the basis of a new process of under-glaze decoration in which the entire piece, color-glaze and body, may be completed in a single burning. Professor Breneman's second paper was entitled "Notes on water analysis." It related to the significance of chlorine in sanitary analyses of water; to the destruction of organic matter by aeration in running streams; to the volume of liquid most suitable for the ammonia titration, the author preferring 100 cc.; and to improvements in the Nessler test.

Next came two papers by Professor Atwater, one on the determination of sulphuric acid, the other on the quantitative estimation of fats; and a communication by E. L. Nichols on "Salt solutions and the absorption of gases." Professor Munroe followed with a paper upon "The action of vegetable acids on tin," in which he showed that the metal in question is acted upon and dissolved by such acids as are found in fruits. Cider which had been kept for a short time in a tin fountain contained 117 milligrammes of tin to the litre. Fruits canned in tin become contaminated with it, and have produced poisoning. He found also that tin reduces lead from its solutions in these acids, excepting acetic acid, and he suggested that our tin culinary utensils had probably protected us to some extent from lead poisoning. Specimens of block tin pipe were shown which had been acted upon by well water, an action which Professor Munroe attributed to humic and ulmic acids.

Papers were also presented by William McMurtrie "On the deficiencies of meteorological work in data of value to agriculture, and the means for supplying them"; by W. Colegrove, on "The direct combination of hydrogen and nitrogen"; by G. F. Kunz, on "The density of a large diamond"; and by L. P. Kinnicutt on

"The substitution of cones made from parchment paper for platinum cones in Bunsen's process of filtration."

Wednesday, September 1st, was the closing day of the meeting. Before the chemists four papers were read by Professor Atwater, and one by C. F. Mabery, on "The crystallographic determination of the form of mucobromic ethyl ether." Professor Atwater's papers were as follows: "The chemical composition and nutritive values of fish"; "The determination of nitrogen by the hypobromite process"; "Some new forms of apparatus," and "The determination of phosphoric acid by the molybdic process." The paper upon fish gave the results of an investigation made for the United States Fish Commission, and included analyses of a large number of specimens of the more common edible species. Some of the percentages of edible solids in various kinds of fish are as follows. The whole fish as sold in the market, waste and all, is put at 100.

Flounders	7.1	Shad	14.8
Cod	10.5	"	18.7
Mackerel	11.4	Lake trout	13.6
Halibut, lean	15.6	Salmon	25.6
" fatter	27.2		

There is no evidence to show that the flesh of fish is richer in phosphorus than other meats are, nor that, if it were so, it would be on that account more valuable for brain food.

In closing this report, reference may properly be made to an account read before the geologists of the Association by Professor C. H. Hitchcock, on the occurrence of tin ore at Winslow, Maine. The locality was described, specimens of cassiterite from it were exhibited, and a bar of tin made from the ore, weighing fourteen ounces, was shown. Professor Hitchcock considers the locality the most promising for tin yet discovered in this country.

F. W. CLARKE.

NOTES.

Ozone in the Air.

For many years the question concerning the occurrence of ozone in the air has been regarded as satisfactorily answered, and little doubt has been expressed regarding its presence. The influence exerted by ozone upon those who breathe it has been discussed very fully; efforts have been made to secure regular systematic observations on the amount of ozone present in the air, and it is safe to say that millions of such observations have been made and many of them recorded. It is hence somewhat startling to find that one of the most careful chemical investigators, one who has acquired an enviable reputation by his painstaking investigations on hydrogen peroxide, E. SCHÖNE, should at this late day seriously question the proofs which have hitherto been adduced for the purpose of demonstrating the presence of ozone in the air. Indeed he feels warranted in stating that "*as yet we possess no chemical reaction by means of which we can prove the existence of ozone in the air.*" The proofs which have been brought forward are mainly those of Schönbein.

Schönbein bases his belief upon three reactions: 1. Something in the air sets iodine free from potassium iodide and caustic potassa is formed. 2. Papers saturated with a solution of manganese sulphate are turned brown in consequence of the formation of Mn_2O_3. 3. Thallium suboxide is oxidized to thallium oxide. But Schöne's investigations have shown that these changes of potassium iodide and thallium suboxide can be effected as readily by hydrogen peroxide as by ozone, and hence the reactions by no means prove the presence of ozone in the air. So also the change of manganese sulphate does not require the presence of ozone, as it is effected by air free from ozone, in which a trace of ammonium carbonate is present; and as this latter substance is normally present in the air, the proof based upon the change of the manganese sulphate papers loses its value. The proofs brought forward by Houzeau and later by Andrews are based indirectly upon the supposed absence of hydrogen peroxide, but since this substance has been shown to be present in the air the proofs are worthless.

The only known reagent by means of which the existence of atmospheric ozone could be positively proved is metallic silver. But no one of the observers mentioned above has ever noticed a blackening of silver in normal air free from sulphur compounds, and Schöne himself has been unable to detect more than the slightest change in color of silver foil exposed for long periods to the action of the air.

As regards the supposed formation of ozone during thunder storms, the odor of the air noticeable under these circumstances is not, as Schöne states, that of ozone, and further it is difficult to see how ozone could be formed by lightning, as the electric *spark* in a mixture of oxygen and nitrogen causes the formation of only hyponitric acid, while the silent discharge is necessary for the formation of ozone. Schöne does not deny that ozone may be present in the air, but simply shows that at present we possess no valid proof of its presence. (*Ber. d. deutsch. chem. Gesell.* 13, 1503.)

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RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

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Rumford Professor in Harvard University.

(Continued from p. 234.)

Twenty-atom Series.—The salts of this series closely resemble those which have been described. I did not succeed in preparing the acid, though I made repeated attempts to do so by mixing sodic tungstate and phosphate together in the proportion of 20 molecules of the former to 2 of the latter, neutralizing with nitric acid, precipitating by mercurous nitrate, and decomposing the mercurous salt by dilute chlorhydric acid. The acid formed always underwent partial decomposition upon concentration, a white crystalline powder being separated while the 24-atom acid was formed. The only well-defined salt of the series which I have obtained is the normal barium compound. From this it will doubtless be possible to obtain others by double decomposition.

Normal 20-atom Barium Salt.—As the baric phospho-tungstates crystallize in general much more readily than the corresponding sodic salts, I employed them to determine what compounds are formed when sodic tungstate and phosphate are mixed in various proportions. To solutions of the two salts in the ratios of 24 molecules of the former to 2 of the latter, of 18 to 2, and of 12 to 2, chlorhydric acid was added until the reaction became just distinctly acid. Baric chloride was then added in excess, and the solutions were quickly filtered from the insoluble white precipitate formed. Beautiful colorless crystals formed, which were readily soluble in hot water, and could be recrystallized without difficulty. These salts proved to have in all cases the same composition, and are represented by the formula

$$20\ WO_5\ .\ P_2O_5\ .\ 6\ BaO+48\ aq,$$

as the following analyses show:

I.

1.1103 gr. lost on ignition with fused borax 0.1458 gr.=13.14 per ct. water.
1.1831 gr. " " " " 0.1560 gr.=13.18 per ct. "
1.0691 gr. gave 0.7775 gr. WO_3 and P_2O_5 =72.72 per ct.
0.9390 gr. " 0.6850 gr. " =72.84 per ct.

II.

1.0676 gr. lost on ignition 0.1400 gr. =13.11 per ct. water.
0.6550 gr. gave 0.4763 gr. WO_3 and P_2O_5=72.72 per ct.

III.

1.1110 gr. lost on ignition 0.1461 gr. =13.15 per ct. water.
0.6409 gr. gave 0.4667 gr. WO_3 and P_2O_5=72.81 per ct.
and 0.0704 gr. $P_2O_{11}U_2$ = 2.18 per ct. P_2O_5
0.6222 gr. gave 0.0710 gr. $P_2O_{11}U_2$ = 2.26 per ct. "

Analyses I were made with the salt from the 24 to 2; II from that obtained from the 12 to 2; and III from the salt of the 18 to 2 mixture. The phosphoric oxide was precipitated twice.

		Calc'd.	Mean.				
20 WO_3	4640	70.67	70.55	70.50	70.62	70.50	70.59
P_2O_5	142	2.17	2.22	....	....	....	2.18 2.26
6 BaO	918	13.99	14.09	....	....	....	....
48 H_2O	864	13.17	13.14	13.14	13.18	13.11	13.15
	6564	100.00	100.00				

The salt dissolves readily in hot water, giving a somewhat milky solution. Chlorhydric acid gives no precipitate at first, but after a time a white crystalline powder is formed, which is the acid salt of the 24-atom series already described.

The fact that the same salt is formed independently of the proportions of sodic tungstate and phosphate is an important one, and illustrates the peculiarities of the series of phospho-tungstates which I have already pointed out.

Eighteen-atom Series.—When normal sodic tungstate and hydrodisodic phosphate are dissolved together in the proportion of 20 molecules of the former to 2 of the latter, and acetic acid is added to the boiling solution until a distinctly acid reaction is obtained, alcohol in excess precipitates a white indistinctly crystalline salt. This dissolves very readily in water, but gives on evaporation a gummy mass, and distinct crystals cannot be obtained. The solution of this salt gives no precipitate at first with salts of potassium, but after a short time beautiful colorless crystals are formed in abundance. The salt dissolves in a rather large excess of water, leaving a small quantity of a white insoluble compound. It crystallizes best from a solution which is not very concentrated, and which is allowed to evaporate spontaneously in the air. The crystals obtained in this way are colorless and well-defined prisms. On re-solution it almost always leaves a small quantity of the slightly soluble salt; but when the whole is dissolved together, the more soluble compound crystallizes without perceptible admixture of the other. From very concentrated solutions I obtained a white granular salt, which, on re-solution in a rather large quantity of water, gave the colorless crystals again.

Of the colorless transparent crystals,

1.1470 gr. gave 0.9372 gr. $WO_3+P_2O_5$=81.71 per ct.
1.5149 gr. " 1.2387 gr. " =81.77 per ct.
1.3494 gr. lost 0.1089 gr. water = 8.07 per ct.
1.5806 gr. " 0.1277 gr. " = 8.08 per ct.
1.1391 gr. gave 0.0498 gr. $Mg_2P_2O_7$ = 2.80 per ct. P_2O_5
1.1856 gr. ". 0.0506 gr. " = 2.93 per ct. "
1.5149 gr. " 0.4738 gr. AgCl =10.26 per ct. potassium.

These analyses correspond to the formula

$$18\,WO_3\,.\,P_2O_5\,.\,6\,K_2O+23\text{ aq},$$

which requires:

		Calc'd.	Mean.		
18 WO_3	4176	78.81	79.12	78.95	79.01
P_2O_5	142	2.68	2.62	2.65	2.58
6 K_2O	566.4	10.69	10.24	....	....
31 H_2O	414	7.82	8.08	8.07	8.08
	5298.4	100.00			

Of the white granular hydrate,

1.3868 gr. gave 1.0985 gr. $WO_3+P_2O_5$=79.21 per ct.
0.9528 gr. " 0.7556 gr. " =79.30 per ct.
1.0396 gr. " 0.0409 gr. $P_2O_7Mg_2$ = 2.57 per ct. P_2O_5
1.0614 gr. " 0.0425 gr. " = 2.56 per ct. "
1.0102 gr. lost on ignition 0.1009 gr. water = 9.99 per ct.
1.7974 gr. " 0.1800 gr. " =10.01 per ct.

The corresponding formula is

$$18\ WO_3\ .\ P_2O_5\ .\ 6\ K_2O+30\ aq,$$

which requires:

		Calc'd.	Mean.		
18 WO_3	4176	76.98	76.84	76.89	76.80
P_2O_5	142	2.62	2.42	2.41	2.42
6 K_2O	566.4	10.44	10.74	....	....
30 H_2O	540	9.96	10.00	9.99	10.01
	5424.4	100.00			

The prismatic and granular salts, therefore, only differ in water of crystallization. It must be remarked, however, that the corrected percentages of the phosphoric oxide in the analyses of the granular salt are too low, which is unusual.

18 : 1 Acid Potassium Salt.—When the normal salt is dissolved in water and chlorhydric acid is added in excess, a white crystalline precipitate is formed, which is but very sparingly soluble in water. Of this salt,

1.2955 gr. gave 1.1828 gr. $WO_3+P_2O_5$=91.30 per ct.
1.3200 gr. " 1.1994 gr. " =90.86 per ct.
1.1390 gr. " 0.0592 gr. $P_2O_7Mg_2$ = 3.32 per ct. P_2O_5
1.5900 gr. " 0.0817 gr. " = 3.29 per ct. "
1.5225 gr. lost on ignition 0.1087 gr. water = 7.14 per ct.
1.1966 gr. " " 0.0856 gr. " = 7.16 per ct.

These analyses correspond to the formula

$$18\ WO_3\ .\ P_2O_5\ .\ K_2O\ .\ 5\ H_2O+14\ aq.$$

		Calc'd.	Mean.			
18 WO_3	4176	87.84	87.93	88.15	87.71	
P_2O_5	142	2.99	3.15	3.17	3.14	corrected.
K_2O	94.4	1.98	1.77	....	....	
19 H_2O	342	7.19	7.15	7.16	7.14	
	4754.4	100.00	100.00			

Ammonium Salt.—The ammonium salt of the 18-atom series may be prepared in the manner given above for the normal potassic compound. When ammonic acetate and alcohol are mixed with a concentrated solution of the sodium salt, no precipitate is formed at first, but after some hours a mass of white crystals is thrown down. After washing with alcohol and re-solution, crystals may sometimes be obtained, but the salt usually forms a nearly colorless gummy mass. In this case white opaque crystals separate from a thick and syrupy mother-liquor. The crystals are soft and gummy to the touch. I did not succeed in obtaining the salt in a state of purity suitable for analysis.

Sixteen-atom Series.—The only representatives of this series which I have obtained are salts of calcium, potassium, and ammonium. They are all well defined and more or less distinctly crystalline.

16 : 1 Acid Calcium Salt.—When calcic tungstate, WO_4Ca, is boiled with a pure dilute solution of phosphoric acid, the salt is dissolved very slowly; but on addition of a few drops of chlorhydric acid, the tungstate passes quickly into solution. The liquid deposits on evaporation colorless, flat, tabular crystals readily soluble in water. Of these crystals,

0.7356 gr. gave 0.6992 gr. $WO_3+P_2O_5=95.05$ per ct.
0.7356 gr. " 0.0399 gr. $P_2O_7Mg_2$ = 3.39 per ct. P_2O_5
1.0347 gr. lost on ignition 0.0366 gr. water = 3.54 per ct.

The phosphoric acid was twice precipitated. The analyses lead to the formula

$$16\ WO_3 . P_2O_5 . CaO . 5\ H_2O+3\ aq,$$

which requires :

		Calc'd.	
16 WO_3	3712	91.56	91.66
P_2O_5	142	3.50	3.39
CaO	56	1.38	1.41 (diff.)
8 H_2O	144	3.56	3.54
	4054	100.00	

16 : 4 Acid Potassium Salt.—In the attempt to prepare the sodium salt to which Scheibler gave provisionally the formula

$$Na_5H_{11}W_6P_2O_{31}+13\ aq,$$

I obtained a thick syrupy liquid, which on dilution with water gave with potassic bromide, after standing a few hours, beautiful colorless needles. The salt is readily soluble in hot water. After recrystallization,

0.5991 gr. gave 0.5000 gr. $WO_3+P_2O_5=83.46$ per ct.
2.1547 gr. " 0.1005 gr. $P_2O_7Mg_2$ = 2.98 per ct. P_2O_5
1.0492 gr. lost on ignition 0.0841 gr. water = 8.01 per ct.

The analyses gave the formula

$$16\ WO_3 . P_2O_5 . 4\ K_2O . 2\ H_2O + 19\ aq,$$

or,

$$W_{16}P_2O_{47}(KO)_8(HO)_4 + 19\ aq,$$

which requires :

		Calc'd.	
16 WO_3	3712	80.53	80.48
P_2O_5	142	3.08	2.98
4 K_2O	377.6	8.19	8.53 (diff.)
21 H_2O	378	8.20	8.01
	4609.6	100.00	

16 : 6 Ammonium Salt.—This beautiful salt was prepared by adding a solution of ammonic chloride to the syrupy liquid obtained by boiling 12:5 sodic tungstate with half its weight of a strong solution of pure phosphoric acid. After standing 12 hours an abundant precipitate of the ammonium salt was formed. This precipitate, after being well drained and twice recrystallized, gave very fine flat prismatic crystals. It is the best-defined ammonium salt which I have obtained. The salt is readily soluble in hot water, and crystallizes as the solution cools. Of this salt,

1.4108 gr. lost on ignition 0.1627 gr. $H_2O + NH_3$ = 11.58 per ct.
{ 0.7705 gr. " " 0.0886 gr. " = 11.49 per ct.
{ 0.7705 gr. gave 0.1243 gr. $P_2O_{11}U_2$ = 3.21 per ct. P_2O_5
0.9629 gr. " 0.1430 gr. NH_4Cl = 7.17 per ct. $(NH_4)_2O$.

The analyses correspond with the formula

$$16\ WO_3 . P_2O_5 . 6\ (NH_4)_2O + 10\ aq,$$

which requires :

		Calc'd.	Mean.			
16 WO_3	3712	85.41	85.28	85.30		85.26
P_2O_5	142	3.27	3.21	....	3.21	....
6 $(NH_4)_2O$	312	7.18	7.17	....	7.17	....
10 H_2O	180	4.14	4.34	4.32		4.36
	4346	100.00	100.00			

14 : 2 Series.—The only compound of this series which I have obtained is a sodium salt with the empirical formula

$$14\ WO_3 . 2\ P_2O_5 . 5\ Na_2O + 42\ aq.$$

I regard this as a double salt, or perhaps as a compound of an 8-atom and a 6-atom salt.

14 : 5 Sodium Salt.—In the communication already referred to,* Scheibler described briefly a sodium salt to which he gave provisionally the formula

$$Na_5H_{11}P_2W_6O_{31}+13\ H_2O.$$

This salt was obtained by boiling 12 : 5 sodic tungstate with half its weight of phosphoric acid. After a short time the salt separates in beautiful crystals. As Scheibler's salt evidently belongs to a 6-atom series, and has therefore a special theoretical interest, I endeavored in various ways to prepare it, but in all cases without success. By boiling 12 : 5 sodic tungstate with half its weight of phosphoric acid I obtained a thick syrupy liquid, which after long standing gave crystals. In another experiment about 75 gr. of the sodium salt were boiled with 13 gr. of syrupy pure phosphoric acid. After dilution and standing for some days, splendid colorless prismatic crystals separated, identical in appearance with those of the last experiment. These were redissolved and recrystallized several times. Of this salt,

0.5551 gr. gave	0.4272 gr. $WO_3+P_2O_5$	=76.95 per ct.	
0.5787 gr. "	0.4459 gr. "	=77.06 per ct.	
1.5430 gr. "	1.1884 gr. "	=77.02 per ct.	
1.0058 gr. "	0.0980 gr. $P_2O_7Mg_2$	= 6.35 per ct.	P_2O_5
1.0285 gr. "	0.1014 gr. "	= 6 34 per ct.	"
1.0023 gr. "	0.3214 gr. $P_2O_{11}U_2$	= 6.38 per ct.	"
1.0152 gr. lost on ignition	0.1656 gr. water	=16.31 per ct.	
1.0240 gr. " "	0.1677 gr. "	=16.37 per ct.	
0.9922 gr. " "	0.1612 gr. "	=16.24 per ct.	

These analyses correspond fairly well to the formula

$$14\ WO_3 \,.\, 2\ P_2O_5 \,.\, 5\ Na_2O+42\ aq,$$

which requires:

		Calc'd.	Mean.			
14 WO_3	3248	70.64	70.65	70.59	70.70	70.66
2 P_2O_5	284	6.18	6.36	6.35	6.34	6.38
5 Na_2O	310	6.74	6.65	....	....	....
42 H_2O	756	16.44	16.34	16.31	16.37	16.34
	4598	100.00				

The phosphoric oxide, which was twice precipitated, is too high, but it may be that in such salts a third precipitation is necessary to effect a perfect separation. I should write the formula of the salt, provisionally, either

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* Berichte der deutschen chemischen Gesellschaft, 5, 801.

$$6\,WO_3 . P_2O_5 . 3\,Na_2O . 3\,H_2O + 8\,WO_3 . P_2O_5 . 2\,Na_2O . 4\,H_2O + 35\text{ aq},$$

or

$$6\,WO_3 . P_2O_5 . 2\,Na_2O . 4\,H_2O + 8\,WO_3 . P_2O_5 . 3\,Na_2O . 3\,H_2O + 35\text{ aq}.$$

There appears to be no reason for distributing the sodic oxide in one way rather than in the other. On the other hand, it is perhaps equally probable that the salt is a compound of two acid salts of a 7-atom series, and that its formula is

$$7\,WO_3 . P_2O_5 . 3\,Na_2O . 3\,H_2O + 7\,WO_3 . P_2O_5 . 2\,Na_2O . 4\,H_2O + 35\text{ aq}.$$

Among the corresponding phospho-molybdates there is at least one series in which the number of atoms of the teroxide is odd. Potassium and ammonium salts in this series have respectively the formulas

$$5\,MoO_3 . P_2O_5 . 3\,K_2O . 3\,H_2O + 4\text{ aq},$$
$$5\,MoO_3 . P_2O_5 . 3\,(NH_4)_2O . 3\,H_2O + 4\text{ aq},$$

if, provisionally, we consider the acid as 12-basic. With respect to the formula given above, and which is that of an acid double salt, I may remark that I shall describe farther on a salt of the 5-atom molybdenum series with the formula

$$5\,MoO_3 . P_2O_5 . 3\,(NH_4)_2O . 3\,H_2O + 5\,MoO_3 . P_2O_5 . 2\,(NH_4)_2O . 4\,H_2O,$$

and that Rammelsberg has already described the corresponding potassium compound. From the general analogy between tungsten and molybdenum, the existence of phospho-tungstates with an uneven number of atoms of tungstic oxide may be fairly inferred from that of phospho-molybdates of the type of the 5-atom compounds above mentioned. I must leave the question undecided, for the present at least, as I have not succeeded in obtaining corresponding salts of potassium, ammonium, strontium or calcium.

The salt crystallizes in long, flat, prismatic forms, and appears to be perfectly homogeneous, so that I believe it should be regarded as a definite compound, and not as a mixture. It is very soluble in water, and crystallizes only from syrupy solutions. It has a strongly marked sweet taste, which is at the same time astringent and very slightly bitter. The solution of the sodium salt gives with potassic bromide a beautiful crystalline precipitate, already described, and having the formula

$$16\,WO_3 . P_2O_5 . 4\,K_2O . 2\,H_2O + 19\text{ aq},$$

and with ammonic chloride, the ammonium salt

$$16\,WO_3 . P_2O_5 . 6\,(NH_4)_2O + 10\text{ aq},$$

also noticed above.

I endeavored to obtain the normal 6-atom sodium salt 6 WO_3. P_2O_5. 6 Na_2O by boiling six atoms of neutral sodic tungstate with the calculated quantity of pure phosphoric acid, but the experiment was unsuccessful.

When a solution of hydro-disodic phosphate is heated, and freshly prepared tungstic oxide is added, in small portions at a time, the oxide is readily dissolved with formation of a colorless or faintly bluish liquid. The solution gave crystalline precipitates with baric chloride and argentic nitrate, but the salts formed proved on analysis to be only mixtures. An ammonium salt was prepared by adding ammonic nitrate and nitric acid to the solution of the sodium salt. The ratio of tungstic to phosphoric oxide in the white crystalline salt formed was as 20 : 1 very closely; but this does not lead to any inference as to the formula of the sodium salt in solution. Tribasic sodic phosphate also dissolves tungstic oxide readily, and the same is true as regards ammonic phosphate; but I could not obtain definite salts from either solution. Potassic phosphate dissolves tungstic oxide very slowly, and only by long boiling. No definite compound was formed in this case.

When hydro-disodic phosphate and tungstic oxide are fused together the latter dissolves and forms a colorless fused mass. This is soluble in water, but, as in the other cases, gives no single well-defined salt. I have made no experiment to determine whether phospho-tungstates of the lower orders dissolve freshly precipitated tungstic oxide so as to form the higher terms in the series. The extraordinary amount of time and labor which I have already spent upon the subject must be my excuse for leaving this and many other interesting points to other investigators. There is no part of the subject which will not amply repay a new and careful study.

Arsenio-Tungstates.

When solutions of alkaline tungstates and arsenates are mixed it frequently happens that white crystalline precipitates are formed, the supernatant liquid becoming strongly alkaline. These precipitates are arsenio-tungstates, and, as might be expected, correspond in a general way to the class of phospho-tungstates already described. They appear to be as a rule less well defined than these last, and, so far as I have been able to discover, exhibit no character of special interest. In analyzing the few salts of this series which I have studied, I have employed the same methods which I have used for the analysis of the phospho-tungstates. Only the conditions are necessarily in some respects different. Arsenic and tungstic oxides were precipitated together by mercurous nitrate, mercuric oxide being employed to secure perfect neutrality. The mercurous salt was then separated upon an asbestos filter, and, after drying, ignited—finally with the blast-lamp—until a constant weight was obtained. In this manner very nearly the whole of the arsenic oxide was volatilized. There is no danger of a reduction to metallic arsenic if the crucible containing the asbestos and precipitate is placed within another, covered, and then cautiously heated. The arsenic oxide is best determined as ammonio-magnesic arsenate, using a large excess of magnesia-mixture in the first precipitation. Two precipitations are necessary to secure a perfect separation; the salt is to be collected on an asbestos filter, and dried in the usual manner. In determining water, or water and ammonia, in these salts, it is best to ignite with a weighed quantity of fused sodic tungstate, as suggested to me by Dr. Gooch; only it must be observed that the fused tungstate is rather deliquescent. With all these precautions fairly good results may be obtained. I endeavored to separate arsenic from tungstic oxide by boiling the salt with dilute phosphoric acid, reducing the arsenic to arsenous acid by sulphurous acid, and then precipitating by sulphydric acid as As_2S_3. This method appears to give a complete separation, but is very tedious and circumstantial.

Acid 3-atom Potassic Arsenio-tungstate.—When 12 : 5 acid potassic tungstate is dissolved, and a solution of potassic arsenate, AsO_4KH_2, is added, a white, very fine-grained precipitate is formed. When an excess of the arsenate is employed, and the mixed solutions are evaporated upon a water-bath, a perfectly white insoluble salt is separated, which is the acid arsenio-tungstate

$$6\,WO_3\,.\,As_2O_5\,.\,3\,K_2O\,.\,3\,H_2O.$$

The formation of this salt may be represented by the equation

$$12\,WO_3\,.\,5\,K_2O + As_2O_5\,.\,K_2O\,.\,2\,H_2O + 4\,H_2O =$$
$$2\,\{\,6\,WO_3\,.\,As_2O_5\,.\,3\,K_2O\,.\,3\,H_2O\,\}.$$

For analysis the salt was washed upon a filter with hot water, then dried upon paper, and afterward—as the mass remained pasty—upon a water-bath, where it finally dried to a hard white mass. Of this salt,

0.8276 gr. gave 0.5902 gr. WO_3 $=71.31$ per ct.
0.7197 gr. " 0.5130 gr. " $=71.28$ per ct.
1.9815 gr. " 0.3841 gr. $As_2O_7Mg_2(NH_4)_2+H_2O$ $=11.73$ per ct. As_2O_5
1.3507 gr. lost on ignition 0.0357 gr. water $=$ 2.64 per ct.

The formula requires:

		Calc'd.		
6 WO_3	1392	71.05	71.31	71.28
As_2O_5	230	11.75	11.73	
3 K_2O	283	14.45	14.33 (diff.)	
3 H_2O	54	2.75	2.64	
	1959	100.00		

The salt dissolves readily in alkaline hydrates. Its chief interest lies in the fact that it serves to establish the existence of a 6-atom series of arsenio-tungstates.

Acid 6:4 Ammonium Salt.—When ammonic arsenate AsO_4NH_4 and neutral sodic tungstate are dissolved together, no precipitate is formed at first, but after a short time a dense white crystalline salt is thrown down, which after twelve hours becomes abundant. Boiling water dissolves this salt readily, but it does not crystallize well from the solution, forming only a thick white mass. If this mass be dissolved in water, nitric acid added in excess gives a white crystalline precipitate, but slightly soluble in the acid liquid and in water. Of this salt, after washing with cold water,

0.8255 gr. gave 0.6013 gr. WO_3 $= 72.84$ per ct.
1.9486 gr. " 0.3980 gr. $As_2O_7Mg_2(NH_4)_2 + H_2O$ $=$ 12.36 per ct. As_2O_5
1.2494 gr. " 0.2635 gr. NH_4Cl $= 10.25$ per ct.

The analyses agree, though not very closely, with the formula

$$6\ WO_3 \,.\, As_2O_5 \,.\, 4\ (NH_4)_2O \,.\, 2\ H_2O + 3\ aq.$$

which requires:

		Calc'd.	
6 WO_3	1392	72.50	72.84
As_2O_5	230	11.98	12.36
4 $(NH_4)_2O$	208	10.83	10.25
5 H_2O	90	4.69	4.55 (diff.)
	1920	100.00	

The differences are, I think, not greater than may be expected in cases in which the salt analyzed cannot be purified by recrystallization.

Normal 16 : 6 Silver Salt.—I obtained this salt by the following process: 100 gr. neutral sodic tungstate and 25 gr. arsenic acid were dissolved together and the solution boiled for some time, then filtered and evaporated upon a water-bath. After a day much sodic arsenate separated in crystals. The filtrate from these crystals deposited a white indistinctly crystalline mass. This was redissolved and potassic bromide added in excess, when an abundant white crystalline fine-grained precipitate was thrown down, which was drained on the filter-pump, and then washed with cold water. This was dissolved in much boiling water, and argentic nitrate added, when a white crystalline salt was thrown down mixed with brownish-red crystals of argentic arsenate. The mass was treated with very dilute nitric acid, which readily dissolved the arsenate, the undissolved portion appearing under a lens as made up of opaque, white, acicular crystals. These were well drained, washed with cold water, and dried on paper by pressure, when the mass showed a faint yellowish tint. The salt is but slightly soluble in cold water. Of this salt,

0.7488 gr. gave	0.5024 gr. WO_3	= 67.09 per ct.
0.7531 gr. "	0.5067 gr. "	= 67.29 per ct.
2.0321 gr. "	0.6147 gr. AgCl	= 24.45 per ct. Ag_2O
1.0215 gr. "	0.3096 gr. "	= 24.48 per ct. "
0.9209 gr. lost on ignition	0.0340 gr. water	= 3.69 per ct.

The analyses correspond tolerably well to the formula

$$16\,WO_3 \,.\, As_2O_5 \,.\, 6\,Ag_2O + 11\,aq,$$

which requires:

		Calc'd.	
16 WO_3	3712	67.10	67.09 .... 67.29
As_2O_5	230	4.16	.... 4.65 (diff.)
6 Ag_2O	1392	25.16	24.45 .... 24.48
11 H_2O	198	3.58	.... 3.69 ....
	5532	100.00	

I do not place implicit confidence in the formula given, as the two determinations of argentic oxide are too low. It is very possible that the salt was slightly decomposed by the dilute nitric acid employed to remove the arsenate. But in any case it is proved that arsenio-tungstates exist in which the ratio of WO_3 to As_2O_5 is higher than 6 : 1, and a method of obtaining such compounds is pointed out.

General Conclusions.—The general results of my investigation of the phospho-tungstates may be stated briefly as follows:—

1. The phospho-tungstates form a series of which the lowest term probably contains six atoms of tungstic to one of phosphoric oxide, and the highest, twenty-four atoms of tungstic to one of phosphoric oxide.

2. At least the greater number of phospho-tungstates contain an even number of atoms of tungstic oxide. The homologizing term for these cases is therefore $2\ WO_3$.

3. The highest number of atoms of base observed in any case is six (old style), which implies that the acid contains twelve atoms of hydroxyl.

4. In all cases observed the number of atoms of hydroxyl replaced by a monatomic metal is even.

5. One instance occurs in which two acid phospho-tungstates of different orders appear to unite to form a definite compound; but this case admits of a different explanation.

6. In all phospho-tungstates studied the number of atoms of base or of hydroxyl is more than sufficient to saturate the phosphoric oxide present, if we admit that the acid is 12-basic. At least a part of the hydroxyl or base must therefore be united to tungstic oxide.

For greater facility of comparison I have brought together the formulas of all the compounds described in this paper, writing them both with the old and the new notation.

$24\ WO_3 . P_2O_5 . 6\ H_2O+47$ aq	$W_{24}P_2O_{71}(HO)_{12}+47$ aq
$24\ WO_3 . P_2O_5 . 6\ H_2O+34$ aq	$W_{24}P_2O_{71}(HO)_{12}+34$ aq
$24\ WO_3 . P_2O_5 . 6\ H_2O+55$ aq	$W_{24}P_2O_{71}(HO)_{12}+55$ aq
$24\ WO_3 . P_2O_5 . 2\ Na_2O . 4\ H_2O+23$ aq	$W_{24}P_2O_{71}(NaO)_4(HO)_8+23$ aq
$24\ WO_3 . P_2O_5 . 3\ K_2O . 3\ H_2O+8$ aq	$W_{24}P_2O_{71}(KO)_6(HO)_6+8$ aq
$24\ WO_3 . P_2O_5 . 3\ K_2O . 3\ H_2O+14$ aq	$W_{24}P_2O_{71}(KO)_6(HO)_6+14$ aq
$24\ WO_3 . P_2O_5 . 3\ (NH_4)_2O . 3\ H_2O+26$ aq	$W_{24}P_2O_{71}(NH_4O)_6(HO)_6+26$ aq
$24\ WO_3 . P_2O_5 . 3\ BaO . 3\ H_2O+43$ aq	$W_{24}P_2O_{71}(BaO_2)_3(HO)_6+43$ aq
$22\ WO_3 . P_2O_5 . 2\ K_2O . 4\ H_2O+2$ aq	$W_{22}P_2O_{65}(KO)_4(HO)_8+2$ aq
$22\ WO_3 . P_2O_5 . 3\ (NH_4)_2O . 3\ H_2O+18$ aq	$W_{22}P_2O_{65}(NH_4O)_6(HO)_6+18$ aq
$22\ WO_3 . P_2O_5 . 2\ Na_2O . 4\ H_2O+5$ aq	$W_{22}P_2O_{65}(NaO)_4(HO)_8+5$ aq
$22\ WO_3 . P_2O_5 . 4\ BaO . 2\ H_2O+39$ aq	$W_{22}P_2O_{65}(BaO_2)_4(HO)_4+39$ aq
$20\ WO_3 . P_2O_5 . 6\ BaO+48$ aq	$W_{20}P_2O_{59}(BaO_2)_6+48$ aq
$18\ WO_3 . P_2O_5 . 6\ K_2O+23$ aq	$W_{18}P_2O_{53}(KO)_{12}+23$ aq
$18\ WO_3 . P_2O_5 . 6\ K_2O+30$ aq	$W_{18}P_2O_{53}(KO)_{12}+30$ aq
$18\ WO_3 . P_2O_5 . K_2O . 5\ H_2O+14$ aq	$W_{18}P_2O_{53}(KO)_2(HO)_{10}+14$ aq

$16\ WO_3 . P_2O_5 . CaO . 5\ H_2O+3\ aq$	$W_{16}P_2O_{17}(CaO_2)(HO)_{10}+3\ aq$
$16\ WO_3 . P_2O_5 . 4\ K_2O . 2\ H_2O+19\ aq$	$W_{16}P_2O_{17}(KO)_8(HO)_4+19\ aq$
$16\ WO_3 . P_2O_5 . 6\ (NH_4)_2O+10\ aq$	$W_{16}P_2O_{17}(NH_4O)_{12}+10\ aq$
$14\ WO_3 . 2\ P_2O_5 . 5\ Na_2O+42\ aq$	
$6\ WO_3 . As_2O_5 . 3\ K_2O . 3\ H_2O$	$W_6As_2O_{27}(KO)_6(HO)_6$
$6\ WO_3 . As_2O_5 . 4\ (NH_4)_2O . 2\ H_2O+3\ aq$	$W_6As_2O_{27}(NH_4O)_8(HO)_4+3\ aq$
$16\ WO_3 . As_2O_5 . 6\ Ag_2O+11\ aq$	$W_{16}As_2O_{47}(AgO)_{12}+11\ aq$

In writing these formulas I have assumed that *all* the acids are 12-basic, since it has been shown that there are salts of the sixteen, eighteen and twenty-atom series which correspond with this view. I shall resume the discussion of the subject in connection with the phospho-molybdates, and at the same time examine in detail the question of the existence of a distinct class of pyro-salts of the tungstic and molybdic series.

(*To be continued.*)

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.

ESTIMATION OF ALKALOIDS BY POTASSIUM MERCURIC IODIDE.

By Albert B. Prescott.

In 1862, Ferdinand F. Mayer, of New York, reported* the uses of a standard solution of mercuric iodide with excess of potassium iodide, in a method of volumetric determination of the chief natural alkaloids. The standard solution was a "decinormal," or, taking Hg at 200, a twentieth normal solution of ($HgCl_2+6KI$), and has been generally known as Mayer's solution, in use for qualitative as well as quantitative purposes. Mr. Mayer so far extended his investigation that, for twelve alkaloids, he stated the number of milligrams of alkaloid precipitated by a cubic centimeter of his standard solution. These volumetric factors coincided with mole-

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* Pro. Am. Phar. Asso. 1862, 238; and again, more fully, Chem. News. 7, 159, April 4, 1863, and, on opium alkaloids, Ibid. 8, 177, 189, Oct. 10, 17, 1863. Am. Jour. Phar. 35, 20. Zeitsch. an. Chemie, 2, 225 (1863). Jahresbericht der Chemie, 1863, 703.

cular quantities, proposed by theory and approved by experiment. The stated quantity of each alkaloid represented its equivalent weight, or the half its equivalent weight, or the whole or the third of twice its equivalent weight. The general correctness of the factors declared by Mayer has obtained frequent confirmation, though, as will be specified further on, some of his numbers have been found to require adjustment, irrespective of molecular quantities, and the combining numbers of some of the alkaloids of his list have become unsettled. Moreover, it has been found that the proportion of alkaloid to iodomercurate is in many cases varied by conditions, so that limits of dilution, time, temperature, etc., need to be prescribed. As a working process there still lacks an indicator for the end of the reaction,—one recommended by Mr. Mayer being palpably fallacious. Another demand for more investigation of the subject lies in apparent discrepancies between the volumetric factors of precipitation and some gravimetric analyses of the precipitates. Upon several of these questions I have at various times obtained some work, reaching as yet few conclusive results, but which may serve even now, with a careful study, to put the subject and its deficiencies in a more tangible shape.

A few years before Mr. Mayer's report, Thomas B. Groves, of Weymouth, England, communicated an investigation "On Some Compounds of Iodide and Bromide of Mercury with the Alkaloids."* Mr. Groves obtained his compounds by precipitation with "a solution of three equivalents of iodide or bromide of potassium, and one equivalent of chloride of mercury" [Hg=100], that is, the constituents of the reagent afterward standardized for volumetric use by Mr. Mayer. Mr. Groves introduces the alkaloidal mercuric iodides, etc., as a class of compounds which he believes has not hitherto been noticed, but in fact the qualitative reaction of alkaloids with solution of iodide of mercury and potassium had been communicated some time before. It is referred to in Gmelin's Hand-book, among the combinations of metallic iodides.† A. von Planta-Reichenau, in a good compilation on the reactions of alkaloids, presented as a dissertation at Heidelberg‡ in 1846, accords potassium mercuric iodide a prominent place among the general

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*Quar. Jour. Chem. Soc. 11, 97, 188 (1859). Phar. Jour. Trans. 18, 181. Jahresbericht der Chemie, 1858. 363. Am. Jour. Phar. 36, 535.

†Cavendish Edition, 2 (1849), 184.

‡Das Verhalten der wichtigsten Alkaloide gegen Reagentien, S. 41.

reagents for these bases. Mayer credits the first report of the use of potassium mercuric iodide as a qualitative reagent for alkaloids to F. L. Winckler, in 1830.

Mr. Groves made precipitates from solutions of "one equivalent of alkaloid," in salt and with some excess of mineral acid, and "three equivalents of iodide (or bromide) of potassium" with "one equivalent of chloride of mercury," and then made quantitative determinations of the mercury and the iodine of these precipitates. In these analyses, a dried and weighed portion of the [washed] precipitate was dissolved in boiling alcohol, and the solution treated with an excess of fresh ammonium sulphide, to precipitate the mercury as sulphide. The solution was kept hot, slightly acidulated with nitric acid, and the mercuric sulphide separated and weighed. The filtrate was warmed to expel all hydrogen sulphide, and treated with solution of silver nitrate, for the gravimetric determination of the iodine. The difference was estimated as alkaloid. Mr. Groves reported the precipitates as perfectly crystallizable, from hot water or hot alcohol, but did not take the crystalline form for analysis. He made analyses of the precipitates of morphine, strychnine, quinine, and cinchonine. In duplicate operations the results agreed with each other fairly, the variations of iodine percentage being from 0.17 per cent. to 0.82 per cent. of the compound. The results are given in support of the general formula (translating Hg to 200), $AlkHgI_3$. This would be generally referred to the rational form, $AlkHIHgI_2$. However, the formula is not very well supported by the results. By computing the percentages of alkaloids for Mr. Groves' formulae, we obtain:

		Calculated.	Found.				
Morphine in	$C_{17}H_{19}NO_3HgI_3$,	32.91	35.99	mean, from	35.97	and	36.02
Strychnine in	$C_{21}H_{22}N_2O_2HgI_3$,	36.50	33.03	"	33.20	"	32.87
Quinine in	$C_{20}H_{24}N_2O_2HgI_3$,	35.80	30.14	"	30.40	"	29.88
Cinchonine in	$C_{20}H_{24}N_2OHgI_3$,	34.64	29.08	"	28.56	"	29.60

Mr. Groves remarks that the obtained percentages of quinine and cinchonine correspond to molecular weights one-fourth less than those received.

A few months ago I obtained some determinations, by Messrs. FRANK E. JUDSON and CHARLES E. PAYNE, of the percentages of iodine and mercury, in the iodomercurates of several alkaloids, namely: strychnine, morphine, quinine and berberine. The analyses were done a little differently from those by Mr. Groves. The alkaloid precipitate was dried at 100° C., and a weighed portion dissolved in hot alcohol. It was found that the strychnine precipitate could be dissolved by acidulating the hot alcohol with sulphuric acid. Nitrate of silver solution was then added to precipitate the iodine, and the precipitate washed on the filter with hot water (dissolving out any silver sulphate precipitated by the alcohol), dried at 100° C., and weighed. The filtrate was treated with hydrochloric acid (in but slight excess), and the silver chloride filtered out, when this filtrate was charged with washed hydrogen sulphide gas, and the resulting mercury sulphide washed, dried at 100° C., and weighed. Having the iodine and the mercury, the fraction of hydrogen for the HI of the assumed formula was added, and the difference placed as alkaloid. Triplicate operations were made. The analysis of *the strychnine precipitate* gave the following results, placed parallel with centessimals calculated from a molecular formula, and with the mean of Groves' percentages:

	Calculated from $C_{21}H_{22}N_2O_2HIHgI_2$.		Judson & Payne.				Groves.
			1st.	2d.	3d.	Mean.	Mean.
Iodine	381	41.59	40.70	40.69	40.00	40.46	44.19
Mercury	200	21.83	18.50	19.60	21.20	19.77	22.78
H of HI	1	00.11	...	...	...	00.11	...
Strychnine	334	36.47	...	...	...	39.66	33.03
	916	100.00				100.00	100.00

These results, in absence of direct determinations of the alkaloid raise the question whether the iodomercurate of strychnine, as a precipitate, may not be in some degree complex and variable. This precipitate is one of the least soluble of the iodomercurates, according to Mayer, being obtained in a solution containing 1-150,000th of strychnine. The end of the reaction is distinct, and the precipitate settles fairly in acidulated water, but better in concentrated solution of potassium chloride.* In this solution, Dragendorff found each cc. to dissolve 0.00216 gram of the precipitate. Without potassium chloride, 0.1127 gram of strychnine lost 0.0021 gram in precipitating, washing, and estimating from the formula above assumed.† From these gravimetric experiments it

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* Dragendorff: Werthbestimmung starkwirkender Droguen (1874), 62, 69.

† Ibid. p. 68. Strychnine 0.1127 gram, with 7.5 cc. of Mayer's solution (an excess of 0.8 cc.), gave a precipitate of 0.3033 gram. Then 0.3033 × 36.47 = 0.1106, strychnine obtained.

appears that the precipitate in question must consist mainly, and may consist wholly of double iodide of the formula

$$C_{21}H_{22}N_2O_2HIHgI_2.$$

The volumetric factor of 0.0167 gram strychnine ($\frac{1}{20000}$ of $C_{21}H_{22}N_2O_2$ in grams), for 1 cc. Mayer's solution (containing $\frac{1}{20000}$ of HgI_2+4KI in grams), is well established. I have several times obtained its verification with pure crystallized alkaloid. Dragendorff quotes experiments confirming the ratio.* Now our understanding of the chemical equation, in the formation of these alkaloid iodomercurates, must depend upon the composition of the precipitate, as we have little knowledge of the chemical composition of potassium mercuric iodide solutions. As a proposition, we may take this equation:

$$(C_{21}H_{22}N_2O_2)_2H_2SO_4+2(KIHgI_2+3KI)=$$
$$2C_{21}H_{22}N_2O_2HIHgI_2+K_2SO_4+6KI.$$

This presupposes the following formation of Mayer's solution:

$$HgCl_2+6KI=KIHgI_2+3KI+2KCl.$$

The conditions of mixture of Mayer's solution seem to deny that it holds three molecules of *free* potassium iodide (as we have to specify, further on). Nevertheless, some experiments in support of the above equations may be cited. A certain quantity (varied by temperature) of mercuric chloride may be added to Mayer's solution before a permanent red precipitate is attained. If, now, the solution just saturated with mercuric chloride, and containing the least perceptible precipitate of mercuric iodide, be treated with strychnine acidulated solution nearly to completion of the precipitate, and this be filtered out, the filtrate will not bear the least addition of mercuric chloride without production of a red precipitate of iodide of mercury. That is to say, all the iodide which is necessary to hold the mercuric iodide in solution, enters into the precipitate of alkaloid mercuric iodide. The indication is that none of the iodide belonging to the potassium mercuric iodide and essential to its solubility, becomes liberated in the precipitation with strychnine salt. These results are not peculiar to strychnine precipitation, as I obtained the same results with quinine, atropine and aconitine. Another test, implying that soluble iodide is not

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* L. c. p. 62. Strychnine 0.0628 gram, in 10 cc. solution, with 5 cc. concentrated potassium chloride solution, required 3.75 cc. Mayer's solution, indicating 0.0626 strychnine.

liberated in the alkaloid iodomercurate precipitation, was made as follows: Mayer's solution was saturated with mercuric chloride (to the point of precipitation), and then treated with excess of quinine (and other alkaloid) acidulate solution, and filtered, when the filtrate would not precipitate mercuric chloride, on its addition in any proportions.

Regarding the iodomercurate precipitation of atropine, Mayer states* that the precipitate is $(C_{17}H_{23}NO_3HI)_2HgI_2$, "one-half the mercury of the test-liquor remaining in solution." He also makes the same remark again, thus,† "The compounds formed are hydriodates of the base with iodide of mercury; in consequence of which [?] a part of the mercury used for precipitation remains in solution." How it could be true that any part of the mercury used for precipitation remains in solution I am unable to understand, and qualitative tests indicate that it is not true. When Mayer's solution is added to alkaloid acidulate solution, not quite to complete precipitation of the alkaloid, and filtered, the filtrate yields no mercury beyond that trace due to the water solubility of the precipitate itself. Charging the filtrate with hydrogen sulphide, the solution is but slightly darkened, with no precipitate, and the same slight darkening is obtained with hydrogen sulphide in the final water washings of the precipitate. (The mercury of Mayer's solution is changed to precipitate of mercuric sulphide by action of hydrogen sulphide, and so is that of the alkaloid iodomercurate precipitates.) This evidence that no part of the mercury of the reaction is left in solution was obtained with quinine, morphine, aconitine and atropine; and obtained, alike, with Mayer's solution as it is, and with Mayer's solution which had been saturated with mercuric chloride.

It certainly appears, then, that all the mercury of a potassium iodide solution, as well as all the iodide essential to the solubility of the same, enter into the precipitates with the alkaloids,—save only such traces as correspond to the solubility of these precipitates. In accord with this conclusion, regarding the iodide, the equation for strychnine precipitation was proposed with $KIHgI_2+3KI$, instead of $(KI)_2HgI_2+2KI$, for Mayer's solution. Now, regarding the mercury—the element never in excess in our reagent—it has to be admitted, when we disprove Mayer's inexplicable statement for the atropine precipitation, that "one-half the mercury of the

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* Chem. News, 7, 161.

† Ibid. 159.

test-liquor remains in solution," we return to an apparent dilemma —a contradiction as to the ratio between atropine and mercury, as follows:

$C_{17}H_{23}NO_3$ to Hg, from *volumetric* indications: Mayer, 0.0145; Dragendorff, 0.0125; Günther, 0.0193; the ratio varied by conditions; the precipitate somewhat soluble.

$2C_{17}H_{23}NO_3$ to Hg, from *gravimetric* indications: Dragendorff, 0.0375 alkaloid giving 0.0379; 0.0375 giving 0.0386; 0.0420 giving 0.0409, etc., quite uniform. (Precipitate : alkaloid : : 100 : 44.9.)

The above atomic ratio for volumetric use is that of 0.0145 atropine to each cc. of the standard solution: $\frac{1}{20000}$ of $C_{17}H_{23}NO_3$ (289) to $\frac{1}{20000}$ of HgI_2+4KI ($HgCl_2$ 271 and KI 996.6). Mayer gave this, theoretical, as the working factor.[*] Dragendorff reports[†] a large number of results, pretty uniform for 0.0125 atropine to each cc of alkaloid, when the conditions were kept as follows: The dilution 350 to 500 parts for one of alkaloid; the Mayer's solution diluted with an equal bulk of water; the addition so slow that the precipitate may crystallize; the end of the reaction found by filtering a few drops and adding thereto a drop of the standard solution, and a correction made by adding 0.00005 gram alkaloid for each cc. of total solution. Günther, using a method of Dragendorff's, reports[‡] 0.0193 to the cc.

For the atomic ratio found in gravimetric analysis of the atropine precipitate, having only half as much mercury to alkaloid as Mayer's volumetric ratio, I can only cite the experiments of Dragendorff,[§] but they seem to be sufficient. The atropine, in acidulate solution of 350 to 400 parts, is precipitated by a slight excess of Mayer's solution, the precipitate left twenty-four hours to subside, well washed, dissolved in alcohol, and this evaporated to dryness at 100° C. Eight trials are reported, with results ranging as quoted above. Mayer gives no data for the formula he states, $(C_{17}H_{23}NO.HI)_2HgI_2$. The discrepancy, then, is to be acknowledged as an admonition to return to further investigation. The

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[*] Ibid. 159, 160.

[†] Werthbestimmung, Seite 20. Also, in part, Dragendorff and Koppe: Zeitsch. an. Chemie, 6, 309 (1867).

[‡] Zeitsch. f. an. Chemie, 8, 476 (1869).

[§] Werthbestimmung, S. 24. Another report may be mentioned: one made by the present writer, in 1876, from the work of Mr. J. R. Little (Am. Jour. Phar. 48, 388; Jahresbericht der Pharmacie, 1876, 525). As the absolute purity of the alkaloid taken was not made certain, the object being that of approximate assay, I could not quote the results as important in this inquiry. In triplicate trial, 0.100 of atropine gave 0.170 of precipitate. The precipitate was simply water-washed and dried.

molecular formula of atropine obtains support from the late synthetic advances of Ladenberg;* but it is an alkaloid liable to decomposition, and consequent impurity, whereby our perplexity may have arisen. Also, the composition of the iodomercurate may change in being washed with water.

In the precipitation of morphine as iodomercurate, it is well established that, when the dilution is 200 parts of acidulate solution for one part of alkaloid, each cc. of Mayer's solution precipitates very nearly 0.020 of morphine crystallized, or 0.019 of morphine anhydrous. The alkaloidal crystals, $C_{17}H_{19}NO_3H_2O=303$, are constant on the water-bath, becoming anhydrous, $C_{17}H_{19}NO_3=285$, at 120° C. The factor, 0.020 to the cc., was given by Mayer, and is sustained by Kubly and Dragendorff, who make the proviso that the dilution should be 200 to 1.†

In trials that I have made with crystallized morphine, I have found the ratio of 0.020 to one cc. to give results coming near to the quantity taken, but apt to fall a little below.‡ The solubility of the precipitate must not be disregarded: in dilutions of 1 to 4000 the reaction does not appear. In the ratio of 0.0202 gram crystallized morphine to the cc., we have $\frac{1}{30000}$ of $2C_{17}H_{19}NO_3H_2O$ for $\frac{1}{20000}$ of (HgI_2+4KI) in Mayer's solution; or 4 molecules of alkaloid for 3 atoms of mercury, indicating for the precipitate,

$$(C_{17}H_{19}NO_3)_4(HI)_x(HgI_2)_3.$$

The following analyses of the precipitate were made by Messrs. Judson & Payne, following the method previously reported—the same used for strychnine:

	Calculated from		Judson and Payne.				Calculated from	
	$(C_{17}H_{19}NO_3)_4(HI)_4(HgI_2)_3$		1st.	2d.	3d.	Mean.	$(C_{17}H_{19}NO_3)_4(HI)_6(HgI_2)_3$	
Iodine	1270	42.13	42.6	43.0	41.7	42.43	1524	46.61
Mercury	600	19.92	17.5	18.0	19.7	18.40	600	18.35
H of HI	4	0.13	...	...	...	0.13	6	0.18
Morph'e	1140	37.82	...	...	...	39.04	1140	34.86
	3014	100.00				100.00	3270	100.00

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* Deut. Chem. Ges. Ber. 12, 941, 944.

† Werthbestimmung starkwirkender Droguen, S. 86. Zeitsch. an. Chemie, 6, 321. Results as follows:

1st,	0.0224	cryst.	morphine	to the	cc.	in feebly	acid	sol.
2d,	0.0221	"	"	"	"	in strongly	"	"
3d,	0.0191	anhyd.	"	"	"	in feebly	"	"
4th,	0.0205	"	"	"	"	in strongly	"	"

‡ The writer's report on Morphiometric Processes for Opium: Pro. Am. Phar. Asso. (1878), 26, 812; Jour. Chem. Soc. (1880), Abstracts, 192.

Groves (*loc. cit.*) obtained a mean of 42.27 per cent. iodine, and 22.74 per cent. mercury, leaving 32.91 per cent. morphine. His proposed formula was $C_{17}H_{19}NO_3HgI_3$.

In comparison, it may be noted that morphine forms $(C_{17}H_{19}NO_3)_2(HCl)_2PtCl_4$, $(C_{17}H_{19}NO_3)(HCl)(HgCl_2)_2$, and $(C_{17}H_{19}NO_3)_4I_6$.

For morphine, then, gravimetric and volumetric experiments, with the test for iodine in the filtrate, admit the following equation:

$$2(C_{17}H_{19}NO_3)_2H_2SO_4+(KI)_4(HgI_2)_3+8KI=$$
$$(C_{17}H_{19}NO_3HI)_4(HgI_2)_3+8KI+2K_2SO_4.$$

In the quinine precipitation, it is stated that one cc. of Mayer's solution precipitates 0.0108 gram of anhydrous alkaloid. I am unable to cite any volumetric determinations in support of this ratio. The anhydrous alkaloid is obtained at 125° C. The crystallization water of the sulphate is not uniform. The factor 0.0108 is $\frac{1}{20000}$ of two-thirds the molecular weight, 324, and indicates the molecule of the precipitate to be $(C_{20}H_{24}N_2O_2)_2(HI)_x(HgI_2)_3$. The percentages obtained by Messrs. Judson and Payne do not accord with this formula, whether we take two, three, or four of (HI). The following is a comparison of one of these formulae:

	Calculated from $(C_{20}H_{24}N_2O_2)_2(HI)_3(HgI_2)_3$		Judson and Payne.			
			1st.	2d.	3d.	Mean.
Iodine	1143	47.74	47.10	48.30	47.80	47.73
Mercury	600	25.06	20.90	20.10	19.60	20.20
H of HI	3	0.13	...	...	...	0.13
Quinine	648	27.07	...	...	...	31.94
	2394	100.00				100.00

Some time since, a determination of the weight of iodomercurate precipitate of quinine, made by Messrs. Johnston and Lobb, was reported by the writer.* The quinine taken was dried, from the trihydrate, at 100° C. The precipitate was washed, and dried at 100° C. There were obtained,

1st, from 0.280 of quinine, 0.801 of iodomercurate.
2d, " 0.280 " " 0.824 " "
3d, " 0.280 " " 0.812 " "
Mean," 1.000 " " 2.900 " "

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*Am. Jour. Phar. 49, 482 (Oct. 1877); Jahresbericht der Pharmacie, 1877, 419; Phar. Jour. Trans. [3], 8, 407.

If we accept the proportion of 4.28 per cent. of water retained in quinine hydrate dried on the water-bath (Allen, referred to, *Ibid.*), we have 2.485 of precipitate from 1.000 of anhydrous quinine; or 33.01 per cent. of alkaloid in the precipitate, against the 31.94 per cent. of Judson and Payne. Groves* obtained a mean of 23.25 per cent. of mercury; and 46.60 per cent. of iodine, in the precipitate.

From the berberine precipitate, Messrs. Judson and Payne obtained a mean of 4.17 per cent. (40.8, 41.0, 37.7) of iodine; and a mean of 7.73 (7.5, 7.7, 8.0) per cent. of mercury; leaving a mean of 52.10 per cent. of alkaloid. In 1876 I reported† some results of work by Mr. Beach, giving very nearly 2 parts iodomercurate from one part of berberine. Excess of the standard solution did not vary the weight of the precipitate.

Certainly it is desirable to have analyses of these precipitates with direct estimations of the alkaloids in them. Otherwise, the question of hydration is unsettled. The quantity of precipitate made from a solution of a unit of alkaloid becomes an uncertain datum, in most cases, owing to a degree of solubility of the precipitate.

Some determinations of *the proportions of iodide and mercuric salt* needful for solutions were made by Mr. HUGO LUPINSKI,‡ and should be here reported. Four twentieth-normal solutions were made, as follows:

No. 1. Mercuric chloride, 13.55; potassium iodide, 33.22; water to one litre. $HgCl_2 + 4KI = HgI_2 + 2KI + 2KCl$. Some red mercuric iodide remained undissolved. This dissolved when heated, and crystallized on cooling.

No. 2. Mercuric chloride, 13.55; potassium iodide, 33.22; potassium bromide, 2.9825; water to one litre.

$$HgCl_2+4KI+\tfrac{1}{2}KBr=HgI_2+2KI+\tfrac{1}{2}KBr+2KCl.$$

Complete solution required heat, and on cooling there was a crystalline deposit of red iodide of mercury.

No. 3. Mercuric chloride, 13.55; potassium iodide, 33.22; potassium bromide, 5.965; water to one litre.

$$HgCl_2+4KI+KBr=HgI_2+2KI+KBr+2KCl.$$

Dissolved readily and did not deposit on standing four weeks.

Solution No. 3 was used, with the idea that it furnished potas-

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* Jour. Chem. Soc. 11, 101.

†Am. Jour. Phar. 48, 385; Jahresbericht der Phar. 1876, 524.

‡ Graduation Thesis, Univ. Mich. 1878.

sium mercuric iodide of the more stable composition of $(KI)_2HgI_2$, with no excess of iodide, and in a permanent solution. It was thought that, with most alkaloids, the bromide would not react at all.

Using this solution, No. 3, Mr. Lupinski made a diligent search for *an indicator of the end of the reaction*, with alkaloids. (1) A paper wet with saturated mercuric chloride and dried was used—to reveal the presence of an excess of the standard solution, in estimation of alkaloids. The indicator worked well, except that it was not delicate enough. (2) A solution of potassium and ammonium hydrates; to give the mercurammonium iodide, when excess of the reagent was attained, with alkaloid acidulous solutions. The alkali hydrates react with the alkaloid precipitates, and therefore do not serve. (3) A solution of iodic acid and starch, to show when excess of soluble iodide had been attained. This, too, reacted with the precipitates, and was inoperative.

A proposition was made by Mr. Mayer* to find the end of the reaction, by adding excess of the Mayer's solution, and then "without filtering" titrating back with tenth-normal solution of silver nitrate, using normal chromate of potassium as an indicator, in the common way. Each cc. of the standard potassium mercuric iodide to require 4 cc. of the corresponding silver solution. Mr. Lupinski† calls attention to the essential defect in this plan, that it disregards the accumulation of the potassium chloride of Mayer's solution during the precipitation of alkaloids. Also, the excess of potassium iodide would interfere in the same way. The erroneous results of titrating back with Mayer's solution may be placed before the eye by an equation for the morphine precipitation (given before without statement of the chloride present):

$$2(C_{17}H_{19}NO_3)_2H_2SO_4+3(HgI_2+4KI+2KCl)=$$
$$(C_{17}H_{19}NO_3HI)_4(HgI_2)_3+8KI+6KCl+2K_2SO_4.$$

With no excess of the Mayer's solution, there are still 8KI+6KCl to titrate back with the silver solution. Mr. Mayer offers this use of the silver solution, "where no coloring matters, or substances affecting nitrate of silver are present." On trial, some time ago, I found that some of the alkaloid iodomercurate precipitates gradually decompose silver nitrate, in solution, by contact at common temperatures.

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*Chem. News, 7, 159, April 4, 1863.

† Thesis, before cited.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE ETHERS OF URIC ACID.*

VI.—DIMETHYLURIC ACID.

By H. B. Hill and C. F. Mabery.

Dimethyluric acid is formed when diplumbic urate is heated with methyl iodide according to the general method which one of us has already described† for making the monomethyl compound. The preparation of considerable quantities of pure substance by this method is, however, a matter of some difficulty, and we have found that a close attention to details is necessary to insure success.

The diplumbic urate which we used at first was made according to the directions of Allan and Bensch,‡ by precipitating a boiling solution of plumbic nitrate with dipotassic urate purified by alcohol. Although we heated this lead salt with an excess of methyl iodide at various temperatures (100° to 170°) for different lengths of time (five to ninety hours), we could not succeed in obtaining from it a product which did not contain quite a large percentage of the monomethyl ether. We therefore attempted to effect the separation of the monomethyl and dimethyl compounds by fractional crystallization, or by methods based upon differences in the behavior of their salts; but we were unable to find a method which was at all satisfactory, and, after many experiments, convinced ourselves that it was necessary to obtain from the first a product essentially free from the monomethyl compound.

After a long series of experiments which need not be described in detail, we found that such a product could be obtained from a lead salt made by precipitating with the diplumbic urate a small amount of plumbic hydrate. We have made no experiments to show how small this quantity of plumbic hydrate can be made with safety, as it seemed a matter of little importance. In preparing the lead salt we dissolved uric acid in a potassic hydrate solution of

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* Communicated by the Authors. Proceedings Amer. Acad. Arts and Sciences.

† Proceedings Amer. Acad. Arts and Sciences, 12, 27.

‡ Ann. Chem. u. Pharm. 65, 191.

known strength, using twenty per cent. more potassic hydrate than was theoretically required to form the dipotassic urate, and poured this alkaline solution into a boiling dilute solution of plumbic nitrate. After washing the bulky precipitate with hot water we usually washed with alcohol, and finally with a little ether; partly to facilitate the drying, and partly because the lead salt was in this way obtained in a much more compact and convenient form. After drying at 100° the salt was well powdered and dried at 160°.

In order to insure complete decomposition of the lead salt, which evidently is essential to prevent the formation of monomethyluric acid, we have found it necessary to take a slight excess of methyl iodide, to dilute it with an equal weight of ether, and, after mixing thoroughly with the lead salt, to heat for twenty hours at 165°. We have also found it advantageous to allow the tube to cool after heating for twelve to fifteen hours, and to mix the contents thoroughly by shaking before heating further.

After distilling off the ether and the slight excess of methyl iodide, the solid product of the reaction is extracted with boiling water, and the lead precipitated by hydric sulphide. The solution filtered boiling hot deposits on cooling crystals of dimethyluric acid which may be purified by recrystallization from hot water. In this way we have obtained about fifty per cent. of the theoretical yield of well crystallized product apparently pure. Since monomethyl and dimethyluric acids differ in the amount of carbon they contain only by 3.29 per cent., it is evident that the absolute purity of our product could not be determined by analysis.

Dimethyluric acid crystallizes usually in slender oblique prisms, often concentrically grouped, which contain a molecule of crystal water. From saturated solutions where crystallization takes place at a high temperature we have not unfrequently obtained small, compact, pointed prisms, which contain less water and very possibly are anhydrous. The behavior of both of these forms to polarized light shows that they belong to one of the oblique systems. The acid begins to turn brown when heated to about 340°; at higher temperatures it melts, with decomposition and partial sublimation. It is quite soluble in boiling water, sparingly soluble in cold water, still less so in alcohol, and insoluble in ether. Concentrated sulphuric and hydrochloric acids dissolve it readily, and deposit the greater portion upon dilution.

The slender oblique prisms in which methyluric acid ordinarily crystallizes contain one molecule of water when dried *in vacuo* over sulphuric acid.

0.6067 gram lost at 160° 0.0511 gram H_2O=8.49 per cent.

The formula $C_5H_2(CH_3)_2N_4O_3 . H_2O$ requires 8.41 per cent.

The crystals of the second form were obtained for analysis by evaporating a saturated solution of the acid upon the water-bath, and filtering hot. Although our determinations agree closely with the amount required for a half-molecule of water, it is not impossible that the loss in weight is due to hygroscopic moisture, as was the case with the monomethyl acid.

I. 0.4547 gram substance dried *in vacuo* lost at 160° 0.0196 gram H_2O=4.31 per cent.

II. 0.2651 gram lost 0.0114 gram H_2O=4.30 per cent.

The formula $C_5H_2(CH_3)_2N_4O_3 . \frac{1}{2}H_2O$ requires 4.39 per cent.

The composition of the substance dried at 160° was determined by the following analyses:

I. 0.2747 gram gave 0.1097 gram H_2O and 0.4291 gram CO_2.

II. 0.2022 gram gave 0.0789 gram H_2O and 0.3167 gram CO_2.

III. 0.1393 gram gave 0.0557 gram H_2O and 0.2185 gram CO_2.

IV. 0.3521 gram gave 86 cc. nitrogen at 16° and 756.5 mm. pressure.

	Calculated for $C_5H_2(CH_3)_2N_4O_3$	Found. 1.	2.	3.	4.
C	42.85	42.60	42.72	42.78	...
H	4.08	4.44	4.34	4.44	
N	28.57	...	...	...	28.21

The solubility in boiling water was determined by filtering a boiling saturated solution through a hot-water filter into weighed flasks. After cooling, the flasks were weighed, the contents transferred to platinum dishes, evaporated to dryness, and the residue dried at 165°.

I. 54.2110 grams solution left 0.2043 gram residue.

II. 57.8596 grams solution left 0.2940 gram residue.

The boiling saturated solution contains the following percentages:

1.	2.
0.5152	0.5081

To determine the solubility in cold water a hot solution was kept at 20° for four hours with occasional stirring. The solution was then filtered into weighed platinum crucibles, evaporated to dryness, and the residue heated at 160°.

I. 35.6147 grams solution left 0.0189 gram residue.
II. 25.2221 grams solution left 0.0134 gram residue.
III. 21.9260 grams solution left 0.0116 gram residue.

The solution saturated at 20° contained in percentages:

1.	2.	3.
0.0531	0.0532	0.0529

Taking the mean of these results, dimethyluric acid requires for solution 195.2 parts boiling water and 1885.3 parts of water at 20°.

An aqueous solution has a slight acid reaction, and decomposes carbonates on heating. A solution in sodic or potassic hydrate is not precipitated by carbonic dioxide. From concentrated cold solutions it is precipitated by stronger acids in a gelatinous form; from more dilute solutions it separates in crystals.

SALTS OF DIMETHYLURIC ACID.

Dipotassic dimethylurate.

$K_2C_5(CH_3)_2N_4O_3 . 4H_2O$.

Dimethyluric acid was dissolved in an excess of a dilute solution of potassic hydrate, the clear solution boiled for several minutes, and about ten volumes of alcohol added. The crystalline precipitate, which separated on standing, was filtered off rapidly by the pump, washed with alcohol, and dried *in vacuo* over sulphuric acid and potassic hydrate. This salt crystallizes in fine silky needles, which are very soluble in water. It absorbs carbonic dioxide very rapidly from the air, probably forming the monopotassic salt.

To determine the water of crystallization the salt was heated in a current of dry air, free from carbonic dioxide.

0.8079 gram salt dried *in vacuo* gave 0.1662 gram H_2O=20.57 per cent. Calculated for $K_2C_5(CH_3)_2N_4O_3 . 4H_2O$ 20.92 per cent.

0.3198 gram anhydrous salt gave 0.1766 gram KCl . K=28.95 per cent. Calculated for $K_2C_5(CH_3)_2N_4O_3$ 28.73 per cent.

Monopotassic dimethylurate.

$KC_5H(CH_3)_2N_4O_3 . 1\frac{1}{2}H_2O$.

Potassic carbonate, in slight excess of the theoretical amount, is added to the acid suspended in boiling water. The solution is boiled for some time, and the salt precipitated by adding about ten volumes of alcohol. It is then filtered, washed with alcohol, and dried *in vacuo* over sulphuric acid. The salt crystallizes in branching needles, which are quite soluble in water.

0.2540 gram salt dried *in vacuo* gave 0.0278 gram $H_2O = 10.94$ per cent. Calculated for $KC_5H(CH_3)_2N_4O_3 . 1\frac{1}{2}H_2O$ 10.35 per cent.

0.2180 gram anhydrous salt gave 0.0702 gram KCl. $K = 16.88$ per cent. Calculated for $KC_5H(CH_3)_2N_4O_3$ 16.70 per cent.

Disodic dimethylurate.

$Na_2C_5(CH_3)_2N_4O_3 . 4\frac{1}{2}H_2O$.

This salt is precipitated from a sodic hydrate solution of the acid by alcohol in the same way as the dipotassic salt. It crystallizes in needles much larger than those of the corresponding potassic salt.

0.3064 gram salt dried *in vacuo* gave 0.0780 gram $H_2O = 25.46$ per cent. Calculated for $Na_2C_5(CH_3)_2N_4O_3 . 4\frac{1}{2}H_2O$ 25.23 per cent.

0.2234 gram anhydrous salt gave 0.1074 gram NaCl. $Na = 18.91$ per cent. Calculated for $Na_2C_5(CH_3)_2N_4O_3$ 19.17 per cent.

Monosodic dimethylurate.

$NaC_5H(CH_3)_2K_4O_3 . 2H_2O$.

This salt was made in the same way as the monopotassic salt. It forms microscopic needles which are more soluble in water than the potassic salt.

0.5327 gram salt dried *in vacuo* gave 0.0798 gram $H_2O = 14.98$ per cent. Calculated for $NaC_5H(CH_3)_2N_4O_3 . 2H_2O$ 14.18 per cent.

0.3069 gram anhydrous salt gave 0.0638 gram NaCl. $Na = 10.17$ per cent. Calculated for $NaC_5H(CH_3)_2N_4O_3$ 10.54 per cent.

Dibaric dimethylurate.

$BaC_5(CH_3)_2N_4O_3 . 3H_2O$.

Dimethyluric acid was dissolved in as little boiling water as possible, a solution of baric hydrate added in slight excess of the amount theoretically required, and the solution boiled. The salt separated as the solution cooled, and was purified by recrystallization from hot water. It was filtered rapidly and dried *in vacuo* over sulphuric acid and potassic hydrate. The salt is quite soluble in hot, but slightly soluble in cold water. When cooled rapidly it forms a jelly-like mass, but when cooled slowly it crystallizes in flat, transparent prisms.

0.2177 gram salt dried *in vacuo* gave 0.0307 gram H_2O=14.10 per cent. Calculated for $BaC_5(CH_3)_2N_4O_3 . 3H_2O$ 14.03 per cent.

0.1875 gram anhydrous salt gave 0.1335 gram $BaSO_4$. Ba= 41.86 per cent. Calculated for $BaC_5(CH_3)_2N_4O_3$ 41.89 per cent.

Monobaric dimethylurate.

$Ba(C_5H(CH_3)_2N_4O_3)_2 . 3H_2O.$

This salt was made by boiling an aqueous solution of the acid with baric carbonate, filtering, and precipitating the filtrate with alcohol.

0.3661 gram salt dried *in vacuo* gave 0.0342 gram H_2O=9.34 per cent. Calculated for $Ba(C_5H(CH_3)_2N_4O_3)_2 . 3H_2O$ 9.29 per cent.

0.3350 gram anhydrous salt gave 0.1491 gram $BaSO_4$. Ba= 26.17 per cent. Calculated for $Ba(C_5H(CH_3)_2N_4O_3)_2$ 25.99 per ct.

Further study of the salts of dimethyluric acid seemed to us of no immediate importance, since the results we had reached served to establish beyond all doubt its dibasic character.

Action of Hydrochloric Acid.

Dimethyluric acid, when heated with concentrated hydrochloric acid, is completely decomposed, giving products perfectly analogous to those described by Strecker* as resulting from the decomposition of uric acid, and qualitatively identical with those obtained under the same conditions from methyluric acid.

The dimethyluric acid was heated for several hours with hydrochloric acid saturated at 0° to 170°. The liquid from the tubes, which showed great pressure on opening, was evaporated to dryness on the water-bath, the residue dissolved in water and distilled with plumbic hydrate in a current of steam as long as the distillate gave an alkaline reaction. The distillate was caught in hydrochloric acid, evaporated to dryness on the water-bath, and the residue treated with a mixture of absolute alcohol and ether. Ammonic chloride was left undissolved, while in solution was a salt which gave qualitative tests characteristic of the monamines. The platinum salt, recrystallized from water, gave on analysis:

0.5421 gram left on ignition 0.2261 gram platinum.

	Calculated for $(CH_3NH_2)_2PtCl_6$.	Found.
Pt	41.61	41.75

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* Ann. Chem. u. Pharm. 146, 142; Zeitschr. für Chemie, 1868, 215.

In order to find the relative amounts of ammonia and methylamine which were formed in this reaction, we determined the percentage of chlorine in the saline residue as obtained by distillation with plumbic hydrate. The residue of chlorides was dried at 100° and the chlorine precipitated by argentic nitrate.

0.6365 gram mixed chlorides gave 1.4681 gram AgCl. Cl_2 = 57.07 per cent. Calculated for 2 molecules methylamine chloride and 1 molecule ammonic chloride = 56.50 per cent.

Two molecules of methylamine are therefore formed in the reaction and one molecule of ammonia.

The liquid remaining in the flask, after the distillation, was filtered hot, the lead precipitated as sulphide, and the filtered solution concentrated. On long standing crystals of glycocol separated, which, for identification, were converted into the copper salt by boiling with freshly precipitated cupric oxide, and precipitating the filtered solution with alcohol.

0.4757 gram copper salt lost at 135° 0.0391 gram H_2O.

	Calculated for $(C_2H_4NO_2)_2Cu \cdot H_2O$.	Found.
H_2O	7.85	8.22

0.4291 gram anhydrous salt left on ignition 0.1611 gram CuO.

	Calculated for $(C_2H_4NO_2)_2Cu$.	Found.
CuO	37.55	37.54

The reaction may therefore be written:

$$C_5H_2(CH_3)_2N_4O_3 + 5H_2O = 3CO_2 + NH_3 + 2CH_3NH_2 + C_2H_5NO_2.$$

Oxidation of Methyluric Acid.

By the oxidation of dimethyluric acid with nitric acid we were unable to obtain a crystalline product. Since the crystalline amalic acid would undoubtedly have been formed had the two methyl radicals been attached to the same urea residue, we concluded that our syrupy oxidation product contained methylalloxan, and for its identification converted it at once into the calcic methylalloxanate. We followed closely the method which one of us had already described,* and found to give constant results. Dimethyluric acid was dissolved in the smallest possible quantity of nitric acid of sp. gr. 1.42, the solution diluted with water, and the excess of acid

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* Proceedings Amer. Acad. Arts and Sciences, 12, 33.

neutralized with calcic carbonate in the cold. After the solution was freed as nearly as possible from carbonic dioxide, by allowing it to stand for some time *in vacuo*, it was largely diluted with alcohol, filtered, and the calcic methylalloxanate precipitated by the cautious addition of ammonia. The carbon and hydrogen were estimated in this salt dried at 100° by a combustion in a stream of oxygen, the calcium by ignition with sulphuric acid.

I. 0.2334 gram substance gave 0.2103 gram CO_2, 0.0439 gram H_2O, and 0.0921 gram residue. This residue gave 0.1489 gram $CaSO_4$, equivalent to 0.0611 gram calcic oxide. The residue, therefore, contained 0.0311 gram CO_2.

II. 0.2172 gram gave 0.1401 gram $CaSO_4$.

III. 0.2268 gram gave 0.1448 gram $CaSO_4$.

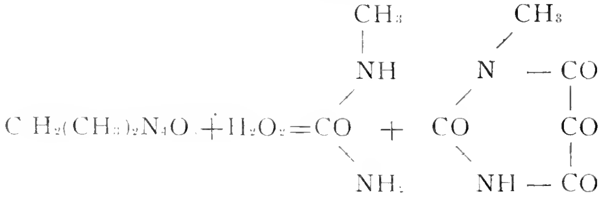
	Calculated for $C_4H(CH_3).N_2O_5Ca$.	Found.		
		1.	2.	3.
C	28.30	28.20		
H	1.88	2.09		
Ca	18.87	18.77	18.97	18.78

In confirmation of these results it seemed advisable to isolate the methylurea which should be formed as the second product of the reaction. We therefore oxidized with hydrochloric acid and potassic chlorate, according to the method of Schlieper, evaporated at a gentle heat until the greater part of the excess of hydrochloric acid was driven off, and then separated from the potassic chloride with absolute alcohol. The residue left by the evaporation of the alcohol at a low temperature gave with nitric acid crystals of methylurea nitrate, which were purified by pressing between folds of paper and recrystallization from water.

0.2464 gram gave 0.1635 gram CO_2 and 0.1147 gram H_2O.

	Calculated for $C_2H_7N_3O_4$.	Found.
C	17.81	18.09
H	5.11	5.15

This reaction may therefore be written:



By the oxidation with potassic chlorate we have, however, invariably observed the formation of a small quantity of a crystalline substance, which we have as yet been unable to obtain in sufficient quantity for investigation. When the residue obtained by evaporation after oxidation was diluted with water, well-formed transparent prisms, pointed at either end, gradually separated, which could be recrystallized from hot water. The quantity formed was extremely small, and, although we modified the process in many ways, we have thus far been unable to increase the yield. At present, therefore, we can do no more than describe the few experiments we have been able to make with the small quantity at our disposal. The substance was readily soluble in hot water, sparingly soluble in cold water or in alcohol. In concentrated nitric acid it dissolved on warming, and crystallized out apparently unchanged on cooling. With ammonia it gave no red color. On heating it melted at about 160°. An analysis gave numbers which correspond more nearly with those required by $C_5H_6N_2O_3$ than by any other simple formula.

0.2078 gram gave 0.3259 gram CO_2 and 0.0788 gram H_2O.
0.1459 gram gave 25.6 cc. nitrogen at 16° and 720 mm. pressure.

	Calculated for $C_5H_6N_2O_3$.	Found.
C	42.26	42.77
H	4.23	4.21
N	19.72	19.27

Although the substance possessed acid properties, we were unable to prepare its salts. On boiling with a solution of baric hydrate it was decomposed with the separation of baric carbonate. In the distillate the presence of ammonia and an amine, without doubt methylamine, could be proved by qualitative tests, and in the residue was an acid whose barium and lead salts were sparingly soluble in water, but which we were unable to identify on account of our very limited supply of material.

By the long-continued action of nitric acid upon dimethyluric acid methylparaban is formed. After boiling with nitric acid of sp. gr. 1.3 till a drop of the solution gave no coloration with ammonia, the solution was evaporated on the water-bath until the excess of acid was driven off and the syrupy residue diluted with a little water. The crystals which separated were pressed with paper and recrystallized from hot water.

Thus prepared the substance melted at 149°, sublimed slowly at 100°, readily at higher temperatures, and gave on analysis the percentages corresponding to methylparaban.

0.2838 gram gave 0.3886 gram CO_2 and 0.0879 gram H_2O.

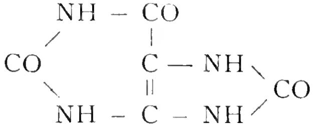
	Calculated for $C_3H(CH_3)N_2O_3$.	Found.
C	37.50	37.35
H	3.13	3.45

By the oxidation of dimethyluric acid with potassic permanganate in alkaline solution, we have been unable to prepare the corresponding dimethylallantoin. The acid either undergoes a more radical decomposition, or more probably the assimilation of water takes place more readily than in case of allantoin or even methylallantoin and the dimethylallantoic acid results.

We made several attempts to isolate from the uncrystallizable product of the oxidation various salts of the dimethylallantoic acid, but found them so uninviting in their character that we could hardly hope to effect their purification.

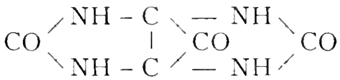
Since considerable time must of necessity elapse before further results can be obtained in this investigation, it may not be out of place to call attention to one inference concerning the structure of uric acid which may fairly be drawn from the facts thus far established.

It has been shown that the two hydrogen atoms of uric acid which are replaced in the formation of salts are directly connected with two different nitrogen atoms; furthermore, when methyl groups are introduced in the place of these hydrogen atoms, that two other hydrogen atoms may then be replaced by metals. The only simple explanation of this behavior would seem to be that the four hydrogen atoms of uric acid are attached to four different nitrogen atoms, and that only two of these hydrogen atoms can be replaced at the same time by strongly basic radicals. Of the many structure-formulae which have thus far been proposed for uric acid, only two contain this arrangement of the hydrogen atoms. These are the formulae of Medicus,*—



* Ann. Chem. u. Phar. 175, 243.

and of Fittig,[*]—



Further discussion of these formulae, or of others fulfilling the same conditions, must be reserved for a subsequent paper.

VII.—RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

ORTHOBROMBENZYL COMPOUNDS.[†]

By C. Loring Jackson and J. Fleming White.

The substances described in this paper are the first substituted benzyl compounds belonging to the ortho series known; unless, indeed, the orthochlorbenzaldehyde, made from salicylic aldehyde,[‡] be included in this class. They were made from the orthobrombenzylbromide,[§] which was described in the first paper of this series as an oily liquid that did not solidify even at —15°. The specimen on which that experiment was tried could not have been perfectly pure, as we have since found that orthobrombenzyl bromide solidifies near zero in large rhombic crystals, often one centimeter in diameter, which melt at 30¼°, and can be recrystallized from alcohol or ligroine. An analysis gave the following result:

0.3570 gr. of substance gave 0.5380 gr. AgBr.

	Calculated for $C_7H_6Br_2$.	Found.
Bromine	64.00	64.13

Orthobrombenzylalcohol, $C_6H_4BrCH_2OH$, was made by the action of aqueous ammonia at 160° in a sealed tube on the acetate obtained by boiling the bromide with an alcoholic solution of sodic acetate. As its melting-point (80°) was much higher than expected, we also prepared it by heating the acetate with alcoholic potassic hydrate in a sealed tube, and by boiling the bromide with water for two days; and found that the products of all these methods melted at

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[*] Grundniss der organischen Chemie, 10th edition, 309.

[†] Presented to the American Academy. Communicated by the Authors.

[‡] Henry, Ber. d. ch. G., 1869, 136.

[§] This Journal, Vol. 1, 100.

the same point (80°), so there can be no doubt that this is the true melting-point of the alcohol. An analysis of the substance made by the first method gave the following results:

0.5543 gr. of substance dried *in vacuo* gave on combustion 0.9131 gr. CO_2 and 0.1990 gr. H_2O.

0.3480 gr. gave, by the method of Carius, 0.3498 AgBr.

	Calculated for C_7H_6BrOH.	Found.
Carbon	44.92	44.94
Hydrogen	3.74	3.99
Bromine	42.79	42 78

Properties. Slightly flattened, white needles, sometimes 5 cm. long, when crystallized from boiling water, from ligroine needles grouped in sheaves, with but little odor, which melt at 80°, sublime in oily drops, and distil with steam very easily. It is very slightly soluble in cold, much more so in hot water or ligroine, and freely in alcohol, ether, benzol, glacial acetic acid, and carbonic disulphide. It can be most conveniently purified by crystallization from hot ligroine. Oxidized with potassic permanganate, it gave orthobrombenzoic acid, melting point 147°–148°.

The *Orthobrombenzylcyanide*, prepared by boiling alcoholic potassic cyanide with the bromide, a dark-colored oil, which did not solidify in a freezing mixture, and seemed to be decomposed by distillation; we therefore did not attempt to purify and analyze it.

The *Orthobromalphatoluic Acid*, $C_6H_4BrCH_2COOH$, was made from the cyanide by heating it with strong hydrochloric acid to 130° in a sealed tube. The product was purified by conversion into the ammonium salt, and recrystallization from water or alcohol of the acid set free from this by dilute sulphuric acid.

It forms white pearly plates, or flattened needles, melting at 102½°–103°; but little soluble in cold, more so in hot water, freely in alcohol, ether, benzol, glacial acetic acid, and carbonic disulphide. It is only sparingly soluble in cold ligroine, but very soluble in hot, from which it crystallizes in small needles arranged in fan-shaped groups.

Argentic Orthobromalphatoluate, $C_6H_4BrCH_2COOAg$, made from the acid by adding ammonic hydrate, driving off the excess of ammonia on the water-bath, and precipitating with argentic nitrate, formed a white mass made up of small needles. It was washed with water, dried *in vacuo*, and analyzed.

0.2686 gr. of the salt gave 0.1200 gr. AgCl.

	Calculated for $C_8H_6BrO_2Ag$.	Found.
Silver	33.54	33.62

It is slightly soluble in boiling water, freely in dilute nitric acid.

Calcic Orthobromalphatoluate, $Ca(C_6H_4BrCH_2COO)_2$, made by boiling an aqueous solution of the acid with calcic carbonate, and evaporating the filtrate, gave, dried *in vacuo*, the following result:

0.24969 gr. of the salt gave 0.0300 gr. CaO.

	Calculated for $(C_8H_6BrO_2)_2Ca$.	Found.
Calcium	8.54	8.58

It crystallizes from a very concentrated hot solution in circular groups of radiating needles, very soluble in water, somewhat less so in alcohol.

The *barium* salt formed an amorphous mass, like varnish.

A solution of the ammonium salt gave the following precipitates: with a salt of copper, *bluish green;* with ferric chloride, *orange brown;* with mercurous or plumbic salts, *white;* all of which resembled those obtained with the parabromalphatoluic acid.

Orthobrombenzylsulphocyanate, $C_6H_4BrCH_2SCN$, is an oil which does not solidify in a freezing mixture of snow and salt. It was not analyzed.

Orthobrombenzylamines. The product of the action of alcoholic ammonia on orthobrombenzylbromide at 100°, for two hours, consisted of crystals of the tertiary amine, and a liquid containing the primary and secondary amines and ammonia, with their bromides. After filtering, the crystals were washed with cold alcohol, sodic hydrate, and finally water, and then recrystallized from warm ether till they gave a constant melting-point (121½°–122°). The filtrate from the crystals was evaporated to dryness, and treated with carbonic dioxide to convert any free primary amine into carbonate. Upon washing with water, the salts of the primary amine and ammonia dissolved, leaving the secondary amine as an oil, which, after washing with sodic hydrate, was converted into the chlorplatinate by addition of chlorplatinic acid to its alcoholic solution. To the filtrate from the secondary amine, sodic hydrate was added, and the oily primary amine thus obtained washed with water until it was free from ammonia, care being taken not to expose it to the carbonic dioxide of the air.

Monorthobrombenzylamine, $C_6H_4BrCH_2NH_2$, is a colorless oil, insoluble in water, but soluble in ether, which absorbs carbonic dioxide from the air very readily, becoming converted into the carbonate.

The *carbonate*, made most easily by allowing an ethereal solution of the free base to evaporate in the air, forms small white crystals; melting-point 95°; and is soluble in water and alcohol.

The *chloride*, made by adding hydrochloric acid to the carbonate, crystallizes in white radiating needles, or from alcohol in small curled needles; melting-point, 208°; and is soluble in water and alcohol.

The *chlorplatinate*, $(C_6H_4BrCH_2NH_3)_2PtCl_6$, is precipitated on adding chlorplatinic acid to the free base; an analysis gave

0.1990 gr. of substance gave 0.0505 gr. Pt.

	Calculated for $(C_7H_6BrNH_3)_2PtCl_6$.	Found.
Platinum	25.16	25.38

It forms indistinct orange-yellow needles, sparingly soluble in water, decidedly so in alcohol, and insoluble in ether.

Diorthobrombenzylamine was made by treating the chlorplatinate with sulphuretted hydrogen, washing the chloride out of the platinic sulphide with hot alcohol, and precipitating the free base with sodic hydrate from the solid chloride. In this way an oil was obtained, which solidified after some time in well-marked rhombic crystals, with an agreeable smell, melting at 36°, and soluble in all the ordinary solvents, with the exception of water.

Diorthobrombenzylamine Chlorplatinate, $[(C_6H_4BrCH_2)_2NH_2]_2PtCl_6$, prepared as already described, was purified by washing with alcohol and water, dried at 70°, and analyzed.

0.5840 gr. of the salt gave 0.1030 gr. Pt.

	Calculated for $[(C_7H_6Br)_2NH_2]_2PtCl_6$.	Found.
Platinum	17.58	17.66

A yellow obscurely crystalline precipitate, slightly soluble in water and alcohol, insoluble in ether.

The *chloride*, made by adding hydrochloric acid to an alcoholic solution of the free base, separates out as the alcohol evaporates, in groups made up of a few radiating white needles, which melt at 166°, are but slightly soluble in cold water, more soluble in hot and in alcohol, sparingly in ether.

Triorthobrombenzylamine, $(C_6H_4BrCH_2)_3N$, gave the following result on analysis:—

0.3245 gr. of substance gave 0.3488 gr. AgBr.

	Calculated for $(C_7H_6Br)_3N$.	Found.
Bromine	45.80	45.73

It forms small prisms with an adamantine lustre, melting at 121½°–122° and subliming in oily drops; almost insoluble in H_2O and alcohol; slightly soluble in cold, freely in hot ligroine, and in ether and benzol.

Triorthobrombenzylamine Chlorplatinate, $[(C_6H_4BrCH_2)_3NH]_2PtCl_6$, made by adding chlorplatinic acid to an ethereal solution of the amine, gave the following result on analysis:

0.3971 gr. of the salt gave 0.0540 gr. Pt.

	Calculated for $[(C_7H_6Br)_3NH]_2PtCl_6$.	Found.
Platinum	13.51	13.60

A whitish yellow, barely crystalline precipitate, insoluble in water and ether, and very slightly, if at all, soluble in alcohol.

On boiling the tertiary amine with dilute alcohol and hydrochloric acid, it dissolved, and on cooling deposited white spheres made up of radiated needles; but an analysis of the substance gave an amount of chlorine too low for the pure chloride, and we did not think the compound of sufficient importance to study it further.

LABORATORY NOTES FROM THE UNIVERSITY OF CINCINNATI.

XV.—THE CONSTITUTION OF THE TARTRATES OF ANTIMONY.

By F. W. Clarke and Helena Stallo.

For many years the so-called tartrates of antimony have been universally regarded as salts in which a peculiar univalent group, SbO, is present as a base. The fact that all of them contain oxygen in excess of that appertaining to the tartaric acid, usually in the ratio of one atom to every atom of antimony, has been the main justification of this view—a view which hitherto has seemed to be almost a necessity. In the following pages we shall endeavor to show that, as far as these compounds are concerned, the hypothesis of any such radicle is wholly superfluous; that all or nearly all of them may be more intelligibly interpreted upon the supposition that they are derived directly from trivalent antimony, and that some of them represent a new acid, of which the above-named metal is a constituent.

The experimental part of our investigation is based upon a fact which has long been known, namely, that when tartar emetic is added to solutions of certain metallic salts, double decomposition ensues and new compounds are precipitated, in which the other metals replace the potassium of the original double tartrate. For example, tartar emetic gives with barium chloride a double salt which is ordinarily represented by the formula $C_8H_8Ba(SbO)_2O_{12} . 2H_2O$. That is, the univalent potassium has exchanged places with the bivalent barium, the tartaric nucleus and the antimony having been transferred together as though they formed a single acid group. The preparation of the complex acid representing this group was the first object of our researches.

A quantity of the barium salt corresponding to tartar emetic having been carefully prepared, it was suspended in water and decomposed by an exactly equivalent amount of dilute sulphuric acid. Barium sulphate was of course thrown down, and, upon filtering, a strongly acid solution was obtained, rich in antimony. At first the filtrate was turbid, a fact which we erroneously attributed to the transmission of finely divided barium sulphate through the filter. We soon found, however, that even the refiltered solution, though perfectly clear at first, soon became milky, and that a sediment was deposited containing antimony. We had then a solution of an antimony compound, though plainly one of decided instability. It proved to be the sought-for acid of which tartar emetic is the potassium salt.

The properties of this acid are in certain respects very remarkable. We have already stated that upon standing it deposits a white precipitate, evidently in consequence of decomposition. The rate of deposition depends upon temperature and the degree of dilution, taking place most rapidly with warmth, and in concentrated solutions. An excess of sulphuric acid instantly brings it about, a point which must be carefully regarded in the preparation of the compound. Upon heating the acid a series of changes occur which we believe to be unique in their character. Below 30°

the solution remains tolerably clear, and the precipitate forms but slowly. At temperatures only a degree or two higher it is deposited most copiously, and assumes a curdy appearance. If now the liquid with the precipitate in it be evaporated to dryness over a water-bath, the white curds gradually disappear, and at last a transparent gummy mass is left. This mass dissolves completely in cold water, regenerating the original acid, which may again be decomposed by warming, reproduced by evaporation to dryness and re-solution, and so on indefinitely. This curious cycle of changes cannot fail to suggest some interesting questions to the student of chemical equilibrium. In no case is the total antimony of the solution present in the white precipitate, even when the latter is thrown down by prolonged boiling. A variable proportion of the metal always remains dissolved.

In order to determine the composition of the acid, a series of experiments, partly qualitative and partly quantitative, were undertaken. Theoretically, from the manner of its formation, it ought to be tartar emetic, with an atom of H in place of the atom of K. In other words, it should have the empirical formula $C_4H_5SbO_7$, a composition which is ordinarily represented by the rational symbol

$$C_4H_4O_6\left\{\begin{array}{l}H\\ SbO.\end{array}\right.$$

As the acid could not be isolated in a definite anhydrous condition, because of its instability, indirect methods of examination had to be employed. To begin with, portions of it were respectively neutralized with the carbonates of potassium, barium, zinc, cobalt, and strontium, all of which dissolved freely. The portion treated with potassium carbonate gave readily crystals of tartar emetic, while that saturated with barium carbonate yielded the characteristic scales of the barium salt from which the acid itself is prepared. With cobalt and zinc carbonates, solutions were obtained which were perfectly clear when hot, but which solidified upon cooling to firm waxy or gelatinous masses. These were purified by re-solution and re-deposition, and dried at 100°. Upon estimating the cobalt and zinc, the percentages came out as follows, agreeing fairly with salts analogous to tartar emetic.

Cobalt salt	Co found,	9.88	Theory,	9.42
Zinc "	Zn "	11.10	"	10.11

Attempts to estimate the antimony in these compounds gave varying results, indicating that the formation of the absolutely pure salts probably depends upon undetermined conditions. The peculiar tendency of the acid to decompose, depositing its antimony, threw great difficulties in the way of preparing any but the most definite and stable of its derivatives. We have, in fact, strong reason to suspect that the carbonic acid evolved by its first action upon a carbonate, brings about a considerable change in its composition; but this point remains to be accurately settled. This suspicion was aroused by the peculiar action of the acid upon strontium carbonate. The solution thus obtained readily deposited rosettes of needles, which, dried by pressure between folds of filter paper, gave the following percentages of water, strontium and antimony. The analyses represent two distinct samples, prepared at different times and from different material.

	I.	II.
Sr	18.69	19.58
Sb	7.20	6.87
H_2O	...	21.90

It will be noticed that here, instead of an atomic ratio of Sr : Sb_2, the ratio is nearly Sr_4 : Sb. This agrees with no readily assignable formula, so that, although we have a clue to the real structure of the salt, we prefer to leave it for further investigation. Suffice it to say for the present that it is undoubtedly a double compound of a tartrate of strontium with a tartrate of strontium and antimony. Whether the latter is analogous to tartar emetic or not is still an open question. The formation of the salt evidently involves a partial decomposition of the acid and a deposition of some of its antimony.

Although the foregoing results with the salts of potassium, barium, cobalt and zinc were tolerably conclusive, another series of experiments was undertaken in order to ascertain whether, in the formation of the acid from the barium compound, the whole of the antimony passes into the filtrate. If it does, then the composition of the acid must be that which is theoretically assigned; if not, the questions involved are unsatisfactorily answered.

A quantity of the barium salt was prepared with every precaution needful to ensure purity, and the percentage of barium in it was accurately determined. The result agreed excellently with the formula of the compound. Several grams of this preparation, containing obviously a known amount of antimony, were then suspended in ice-water and decomposed by an equivalent quantity of very dilute standardized sulphuric acid, added from a burette. After brief agitation the liquid was filtered into a stoppered cylinder containing lumps of ice, and the residue upon the filter was thoroughly washed with ice-water. The filtrate, which was perfectly clear at first but afterward deposited a small amount of sediment, was then diluted to a known volume and divided into five equal parts. In three of these the antimony was determined. The barium sulphate, however, retained a little antimony, a circumstance which could not be altogether avoided. If the sulphuric acid were added in the least deficiency, a part of the barium salt would remain upon the filter undecomposed; if in the smallest excess, a portion of the new acid would be destroyed; in no case could a trifling deposition of the white precipitate, prior to filtration, be absolutely prevented. This series of experiments was twice repeated. The first time, the filtrate contained about seven-eighths of the total antimony. On the second occasion the barium salt was first ground to fine powder in an agate mortar, and the results in the three portions of the filtrate examined were as follows. The figures represent the percentage of the total antimony of the barium salt which went through into solution.

92.62
93.98
92.96

Mean, 93.19

The variations in these values are due to the fact which is above mentioned, that the solution in the stoppered cylinder contained a slight deposit of white precipitate. This rendered it impossible to divide the acid into rigidly equal portions. The results, however, are as favorable as could be expected. The filtrate contains over nine-tenths of the total antimony; and this fact, together with that of the reproduction of the potassium and barium salts from the acid, fixes the empirical composition of the latter, in accordance with the formula $C_4H_5SbO_7$.

As an "acid tartrate of antimony" having the above formula is mentioned in many reference books, we undertook its re-examination in order to see whether it was identical with our acid. The compound in question is attributed to Péligot, who, however, gave no analysis of it. Upon mixing a solution of the hyperacid antimonious tartrate with alcohol he obtained a white precipitate which, after drying at 160°, consisted of $C_4H_3SbO_6$. This, dried at a lower temperature, ought to retain the elements of water, when it would be represented by the formula $C_4H_5SbO_7$. But this formula was not experimentally established. Accordingly we prepared the substance by Péligot's method, only we dried it at 100° instead of at 160°. Unfortunately, we did not get enough of the compound for complete analysis, but two estimates of antimony in it gave the following percentages:

39.27
39.41

Mean, 39.34

The compound $C_4H_5SbO_7$ should contain 42.10 per cent.; for $C_4H_5SbO_7 . H_2O$ the figure would be 39.60. Probably the latter formula is correct, although it needs scrupulous verification. At all events, Péligot's salt is not identical with our acid, for its solution is perfectly stable even upon long boiling. It is quite probable, therefore, though far from certain, that there are two isomeric bodies represented by the empirical formula $C_4H_5SbO_7$.

Upon studying the decomposition of the new acid by heat, highly satisfactory quantitative results were obtained. We have already stated that the white precipitate which is deposited upon warming does not contain the total antimony. No definite portion of the latter remains in solution, however, but a varying quantity, the amount depending upon undetermined conditions of dilution and temperature. Indeed, a part of the precipitate thrown down by actual boiling seems to redissolve upon cooling.

Evidently, the important thing to do was to ascertain the exact composition of this white precipitate. Accordingly, several lots of it were prepared, washed thoroughly, and dried at 100°. The product was a fine white powder, which, upon qualitative examination, proved to be a hydroxide of antimony, of decidedly stable character. Its water is retained even at 150°, and is completely expelled only at a much higher temperature. Its percentage of antimony was determined in two distinct samples and by two different methods. The results were as follows:

First sample	70.58	Weighed as Sb_2S_3
" "	70.45	" " Sb_2O_4
Second "	70.32	" " Sb_2S_3
Mean,	70.45	

A single estimation of water gave an amount corresponding to 1.83 per cent. of hydrogen. Taking oxygen by difference, we get the following composition for the white precipitate, which clearly establishes it as ortho-antimonious acid, $Sb(OH)_3$.

	Found.	Theory.
Sb	70.45	70.18
H	1.83	1.75
O	27.72	28.07
	100.00	100.00

Although ortho-antimonious acid is occasionally referred to upon theoretical grounds, we are unable to find that it has ever before been actually prepared and described. The only antimonious hydroxide of which authentic analyses have been published is that obtained by Schaffner, and to which the empirical formula $Sb_2H_4O_5$ has been assigned. This undoubtedly represents a hydrate of meta-antimonious acid, and may be formulated rationally as $2(SbO \,.\, OH) \,.\, H_2O$. It contains 74.08 per cent. of antimony. The formation of the ortho-antimonious compound from our new complex acid is readily intelligible according to the subjoined equation,

$$C_4H_5SbO_7 + 2H_2O = SbH_3O_3 + C_4H_6O_6.$$

Upon heating the mixture of hydroxide and tartaric acid thus obtained, the two molecules of water are eliminated, and $C_4H_5SbO_7$ is reproduced. We thus have a rational explanation of the curious cycle of chemical changes previously referred to.

As is well known, the addition of one of the stronger acids or alkalies to tartar emetic immediately produces a white precipitate. That which is thrown down by ammonia is said to be antimony trioxide, a fact which we have reverified. The precipitates formed by acids are ordinarily described as "basic compounds," containing both tartaric acid and the precipitant; but we cannot find that they have ever been systematically examined. In this direction we made a few experiments which, though by no means conclusive, suggest considerations different from those that are commonly entertained. We precipitated one portion of tartar emetic with sulphuric acid and another with nitric acid, and, after washing and drying, estimated the antimony in each precipitate. These are our results:

In the H_2SO_4 precipitate, 69.74 per cent.
" HNO_3 " 71.49 "

These figures are quite near the theoretical percentage of antimony in ortho-antimonious acid, and we are therefore inclined to regard both substances as that compound slightly impure. Each precipitate retained only traces of the stronger acid, and a quantity of organic matter which is easily ascribable to deficient washing. If our supposition is correct, the following equation will simply explain the formation of the $Sb(OH)_3$,

$$C_4H_4SbKO_7+HNO_3+2H_2O=C_4H_6O_6+KNO_3+SbH_3O_3.$$

That is, the nitric acid takes away the potassium, forming a nitrate, and setting the new complex acid free. The latter, reacting with water, immediately displays its characteristic instability and undergoes decomposition, a part of the antimony remaining dissolved in the tartaric acid as usual. We have here an explanation of the fact which so puzzled some of the earlier theoretical chemists, namely, that a strong acid added to tartar emetic throws down only a portion, and that a variable portion, of the antimony.

The theoretical considerations suggested by the foregoing experiments are very obvious. We have found that tartar emetic yields an acid of definite constitution, which is certainly different from the acid tartrate of antimony described by Péligot. This acid deposits a hydroxide $Sb(OH)_3$, whereas if it contained an antimonyl group SbO we should expect to get from it meta-antimonious acid SbO . OH. Moreover, the liquid containing its deposit of ortho-antimonious acid readily regenerates the new tartrate in the peculiar manner described. We therefore change the old formula of acid antimonious tartrate,

$$C_4H_4O_6\left\{\begin{matrix}H\\SbO,\end{matrix}\right.$$

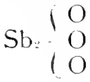
into one representing our compound as derived from ortho-antimonious acid through the replacement of two univalent hydroxyl groups by the bivalent group $C_4H_4O_6$. Thus we have for ortho-antimonious acid, our new tartrantimonious acid and tartar emetic, the following formulae respectively:

$$Sb\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right. \qquad Sb\left\{\begin{matrix}C_4H_4O_6\\OH\end{matrix}\right. \qquad Sb\left\{\begin{matrix}C_4H_4O_6\\OK.\end{matrix}\right.$$

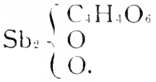
All the other known tartrates of antimony, single and double, with possibly one exception, are capable of equally suggestive interpretations. Of course the remaining tartrantimonites, as we purpose calling the salts analogous to tartar emetic, are formulated similarly to that familiar compound. The so-called neutral tartrate described by Berzelius is ordinarily written,

$$C_4H_4O_6 \left\{ \begin{matrix} SbO \\ SbO, \end{matrix} \right.$$

and its neutrality is assumed. It may with equal propriety be written thus, in comparison with antimony trioxide:



$$Sb_2 \left\{ \begin{matrix} O \\ O \\ O \end{matrix} \right.$$



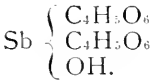
$$Sb_2 \left\{ \begin{matrix} C_4H_4O_6 \\ O \\ O. \end{matrix} \right.$$

The old view represents it as a neutral salt, while the new formula regards it as highly basic. Only experiment can decide which is the better.

The hyperacid tartrate of antimony described by Péligot is commonly regarded as formed by the union of one molecule of the acid tartrate with one molecule of tartaric acid, thus:

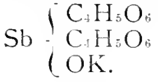
$$C_4H_4O_6 \left\{ \begin{matrix} H \\ SbO \end{matrix} \right. . C_4H_6O_6.$$

We ignore water of crystallization. It may also be written as follows:



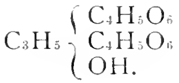
$$Sb \left\{ \begin{matrix} C_4H_5O_6 \\ C_4H_5O_6 \\ OH. \end{matrix} \right.$$

For this formula we at once find a justification in Knapp's acid tartar emetic, $C_4H_4K(SbO)O_6 . C_4H_6O_6$. This becomes



$$Sb \left\{ \begin{matrix} C_4H_5O_6 \\ C_4H_5O_6 \\ OK. \end{matrix} \right.$$

Here then we have a new complex acid derived from ortho-antimonious and tartaric acids, and also its potassium salt. If this view is correct, a new line of investigation is opened up among the tartrates of antimony, and we may reasonably expect to discover a series of compounds analogous in constitution to the well-known glycero-tartaric acids. For example, glycero-ditartaric acid may be written as follows:



$$C_3H_5 \left\{ \begin{matrix} C_4H_5O_6 \\ C_4H_5O_6 \\ OH. \end{matrix} \right.$$

This acid, however, is dibasic, whereas the corresponding antimony compound should have a basicity of three. Such differences are naturally to be anticipated, since antimony is a feebly electro-negative metal, while glyceryl is a distinctly electro-positive group. Ortho-antimonious acid and glycerine, therefore, although peculiarly comparable, are so only within certain limits. The hydroxyl molecules of the one must have different functions as regards basicity from the similar molecules of the other.

By heating the tartrates of antimony to temperatures near 160°, certain compounds are produced, of which the formation may be represented as follows. In no case is the SbO group necessary.

$$Sb_2 \left\{ \begin{matrix} C_4H_4O_6 \\ O \\ O \end{matrix} \right. - H_2O = Sb_2 \left\{ \begin{matrix} C_4H_2O_6 \\ O. \end{matrix} \right.$$

$$Sb \left\{ \begin{matrix} C_4H_4O_6 \\ OH \end{matrix} \right. - H_2O = SbC_4H_3O_6.$$

$$Sb \left\{ \begin{matrix} C_4H_4O_6 \\ OK \end{matrix} \right. - H_2O = SbKC_4H_2O_6.$$

In two of these bodies we encounter the residue $C_4H_2O_6$, of which the best known representative is the tetrabasic lead tartrate. In the other, the trivalent antimony directly replaces three of the hydrogen atoms of tartaric acid. The one compound which we are as yet unable to formulate intelligibly is that described by Knapp as formed from the union of a molecule of tartar emetic with three molecules of acid potassium tartrate. This compound, however, needs careful verification.

Although in all the actually known tartrates of antimony the SbO group is, as we have said, superfluous, there may yet be discovered salts in which it can have a definite existence. For example, we have seen that there may be two isomers bearing the formula $C_4H_5SbO_7$. One of these, our tartrantimonious acid, we have definitely established as an ortho compound. The other, if its existence should be verified, would probably turn out to be a meta-antimonious derivative, containing the meta-group SbO. This supposition suggests that there may possibly be two isomeric series of antimonious tartrates, and points out a wide field for future research.

In conclusion, it is hardly necessary to say that the reasoning which we have applied to the tartrates of antimony applies also to the corresponding compounds of boron, arsenic, chromium, and ferric iron. Each of these elements forms with tartaric acid and potassium, salts analogous to tartar emetic, which are commonly represented as containing radicles similar to the group SbO. These radicles we may now reject, and formulate all such compounds as derived from complex acids constructed upon the tartrantimonious type. That these formulae are simpler, clearer, and less hypothetical than the old symbols, we think there can be no doubt.

XVI.—ON THE RELATIVE STABILITY OF CERTAIN ORGANIC SALTS.

By Miles Beamer and F. W. Clarke.

The barium salts of methylsulphuric acid and its homologues, each containing two molecules of water of crystallization, and all yielding comparable products upon decomposition by heat, afford a very good series for the study of relative stability. Decomposition begins at comparatively low temperatures, proceeds slowly and regularly, and its rate differs with the several compounds.

In our experiments the methyl, ethyl, propyl, isopropyl, isobutyl, and amyl salts were studied. Two grams of each were placed in porcelain crucibles, and heated side by side in an air-bath; so that all were simultaneously exposed to identical conditions of temperature. The source of heat was a gas-flame, controlled by a Bunsen-Kemp regulator. Every set of experiments consisted of several successive heatings; after each one of which the salts were allowed to cool, and their losses of weight were determined. In all, nine series of experiments were made. The first was a set of half-hour heatings through a range of gradually increasing temperatures, and served only for preliminary control. Series two and three were half-hour heatings at 100°, continued until no farther loss of weight ensued. Series four, five, six, seven, and nine were of hour heatings at 100°, while series eight consisted of hour heatings at 110°. In each case heating was continued until for the given temperature the weight of the salts became constant.

In order that our results may be fairly comparable we have expressed our percentages of loss after a somewhat peculiar manner. Each salt, when strongly ignited, leaves barium sulphate, and loses certain volatile products; which, in the case of the amyl compound, amount to 45.96 per cent. of the whole. In each case this total possible loss, which differs with the different salts, is taken as our standard, instead of the actual weight of the substance employed, and to it our percentages are referred. Fifty per cent., therefore, in our computations, means not half of the salt under examination, but half of the quantity which it is capable of losing upon ignition.

The general average of our results for all the heatings made through one hour at 100°, is given in the following table. The numbers in the first column indicate the successive heatings. In the other columns are stated the percentages of loss for the respective compounds, expressed according to the method explained above.

No.	Amyl Salt.	Isobutyl Salt.	Propyl Salt.	Isopropyl Salt.	Ethyl Salt.	Methyl Salt.
1.	18.41	29.69	19.19	42.14	35.22	29.74
2.	35.55	46.88	42.27	43.52	43.33	39.34
3.	41.90	53.10	43.08	44.97	47.86	41.22
4.	58.89	57.38	49.49	45.60	51.16	43.17
5.	65.43	59.81	50.92	46.51	55.60	45.56
6.	69.38	61.99	54.25	47.61	58.33	

It is plainly evident that these figures have no absolute significance, but only a comparative value. They show that at the temperature under consideration the amyl salt has the widest range of loss, and that its decomposition proceeds the most regularly. The isobutyl salt comes next in these particulars, and is followed in proper order by the propyl, ethyl, methyl, and isopropyl compounds. If we consider the maximum losses only, then the order will be the same, except that the ethyl and propyl salts will change places. In short, we may safely infer from the data before us, that with the compounds of higher molecular weight, decomposition begins more slowly, but proceeds farther, than with the lower salts of the series. The isopropyl compound, however, acts somewhat abnormally; losing but little after the first heating. Its rapidity of loss is therefore relatively great; while its range of loss is comparatively small. It would be interesting to compare the isobutyl salt with its normal analogue, but for this purpose material failed us. We prepared a small quantity of the normal alcohol, but could not secure enough to work with.

No attempt was made to determine the effect of mass upon rate of change. Investigations in that direction must be left for some future time.

XVII.—SOME NEW SALTS OF URANIUM.

By F. W. Clarke and Mary E. Owens.

Sodium uranate dissolves readily in the substituted acetic acids, yielding definite salts analogous to the well known sodio-uranic acetate.

Sodio-uranic monochloracetate forms large sulphur yellow prisms containing two molecules of water. The analysis agrees well with the formula $NaC_2H_2ClO_2.2(UO.C_2H_2ClO_2).2H_2O$. Sp. gr., 2.748 at 14°.

		Found.		Theory.
U	39·39	39·49	39·76	39·25
Na	3·95	3·78	3·83	3·74
H_2O	5·83			5·88

The dichloracetate and monobromacetate, like the ordinary acetate, are anhydrous. Both salts form small yellow crystals, those of the monobromacetate being clustered in regular stellate groups. Analytical results are as follows:

Dichloracetate, $NaC_2HCl_2O_2.2(UO.C_2HCl_2O_2)$.

	Found.		Theory.
U	36.15	35·69	35·34
Na	3·47	3·49	3·39

Monobromacetate, $NaC_2H_2BrO_2.2(UO.C_2H_2BrO_2)$.

	Found.		Theory.
U	34·22	33·47	33·85
Na	3·28	3·36	3·24

A solution of the double trichloracetate was prepared, but it dried up to a gummy mass without yielding any crystals.

XVIII.—GRAPHITE FROM DUCKTOWN, TENNESSEE.

By W. L. Dudley and F. W. Clarke.

About two years ago we received from the Ducktown Copper Mine a large mass of mineral which purported to be molybdenite.

Upon examination, however, it proved to be merely graphite, mixed with copper pyrites and various silicates. As graphite has never before been discovered in that locality, and as the occurrence of the mineral in such associations is somewhat unusual, we have thought it worth while to put the fact on record. The purest sample we could find gave us 67.99 per cent. of carbon, and 32.01 of ash. The ash had the following composition:

SiO_2	41.06
Fe_2O_3	26.69
Al_2O_3	20.37
CaO	9.76
MgO	2.04
CuO	trace
Mn_2O_3	"
	99.92

This is nearly an impure iron epidote, the oxygen ratios being approximately $RO : 2R_2O_3 : 3SiO_2$.

ON THE DISTRIBUTION OF ARSENIC IN THE HUMAN BODY IN A CASE OF ARSENICAL POISONING.

By S. W. Johnson and R. H. Chittenden.

A recent case of suspected arsenical poisoning in the State of Connecticut led the proper authorities to demand a chemical examination of the body of the victim, Mrs. Riddle. Accordingly the body, which had been buried nearly a year and a half, was disinterred, and all the internal organs removed separately and placed in sealed glass bottles. The entire body was found in a good state of preservation, and the mucous and other tissues, as well as the different organs, showed a firmness and consistency seldom seen in a body so long buried. On opening the stomach the lining membrane was found quite entire, though naturally much shrunken, while adhering to it was found a quantity of a black substance, which, on examination, proved to be bismuth sulphide, formed probably from bismuth subnitrate, which entered into the composition of a medicine taken by the deceased. Portions of this membrane, freed from all adhering matter by thorough washing with water, showed, scattered over its surface, brownish black stains of bismuth sulphide, while here and there were to be seen yellow stains soluble in ammonia, which, on later examination, proved to be arsenious sulphide. The liver and intestines, which in many places had the appearance of fresh organs, likewise showed the yellow stains, and these, together with the remainder of the internal organs, contained an appreciable quantity of arsenic. As the total quantity of arsenic found at this time (2.3798 grains As_2O_3) was, according to the theory of the defense, within the possible limits of a non-fatal dose to a person accustomed to the use of arsenic, the prosecution ordered a second disinterment, and such a thorough chemical investigation to be made as would show with accuracy the total amount of arsenic contained in the entire body. Accordingly, at the second disinterment, such a dissection was made as would insure a fair estimate of the entire content of arsenic. Twenty-one pounds of tissue from different portions of the body were taken, and each individual part subjected to a separate analysis. The entire body, after the removal of the soft organs, weighed but 55½ pounds, so that nearly one-half of the solid tissue of the body was taken for examination. The method of analysis employed was the one recently described by Chittenden and Donaldson;* a method which allows of the accurate determination of minute quantities of arsenic, and in which the arsenic is weighed in the metallic state. 100 grams of sampled substance were employed for each determination, except in several cases where the amount of arsenic was found to be quite small, and then larger quantities were taken; thus in the brain 300 grams were employed. The sampling of the larger masses of bone and muscle tissue, as well as the small organs, was accomplished by placing the entire portion in a small quantity of nitric acid for several days, which gradually disintegrated it, and afterwards by the aid of a gentle heat speedily reduced it to a thin, pasty mass, capable of being accurately sampled. From the amount of arsenic found in the 100 grams of sampled matter, the content of the entire organ or portion of tissue was calculated.

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* This Journal, vol. 2, p. 235.

Internal Organs.

Substance.	Total Weight.	As_2O_3 Found.	Percentage of As_2O_3.
Stomach and Spleen	514 grams	.05359 gram	.01040 per ct.
Kidneys	80 “	.00660 “	.00825 “
Liver	590 “	.04788 “	.00811 “
One Lung and Heart	441 “	.01454 “	.00329 “
Intestines and Uterus	978 “	.02582 “	.00260 “
One Lung and Liquid from Thorax	402 “	.00583 “	.00140 “
Urinary Bladder, etc.,	73 “	distinct trace	
Brain	477 “	unweighable trace	
	3555 “	.15426 gram	.00433 “
	7 lb. 13 oz., 173.40 grains	2.3805 grains	

Left Arm.

Substance.	Total Weight.	As_2O_3 Found.	Percentage of As_2O_3.
Upper Arm	665 grams	.00542 gram	.00081 per ct.
Fore Arm	288 “	.00158 “	.00055 “
Hand	150 “	.00019 “	.00012 “
	1103 “	.00719 “	.00065 “
	2 lb. 6 oz., 396.71 grains	.11120 grain	

Right Leg.

Substance.	Total Weight.	As_2O_3 Found.	Percentage of As_2O_3.
Leg from Knee to Ankle	1323 grams	.00864 gram	.00065 per ct.
Flesh from Thigh	3160 “	.01635 “	.00051 “
Foot	468 “	.00105 “	.00022 “
Thigh Bone	615 “	.00040 “	.00006 “
	5566 “	.02644 “	.00047 “
	12 lb. 4 oz., 146.84 grains	.40815 grain	

Muscle and Bone Tissue from other parts of the Body.

Substance.	Total Weight.	As_2O_3 Found.	Percentage of As_2O_3.
Transverse section of body above Pelvis	1920 grams	.03011 gram	.00156 per ct.
Muscle and Ribs from left Breast	406 “	.00371 “	.00091 “
Abdominal Muscle, right Side	615 “	.00358 “	.00058 “
	2941 grams	.03740 gram	.00127 “
	6 lb. 7 oz., 324.24 grains	.57715 grain	

Summary of the Examination of Tissue.

	Total Weight.	Total As_2O_3.
Arm	2 lb. 6 oz., 396.71 grains	.11120 grain
Leg	12 lb. 4 oz., 146.84 "	.40815 "
Muscular and Bony Tissue from other parts of the body	6 lb. 7 oz., 324.24 "	.57715 "
	20 17 867.79	1.09650
	21 2 430.29=339 oz.	

The entire body, aside from the internal organs, weighed at the second interment, 55½ pounds=880 oz. Thus the proportion,

339 : 880 : : 1.09650 : 2.8463 grains,

gives with reasonable accuracy the total amount of As_2O_3 contained in the body tissue, and this amount added to that contained in the internal organs, gives a total of 5.2261 grains As_2O_3. In the stomach and spleen were found an amount of bismuth corresponding to .26648 gram of bismuth teroxide; which, on the supposition that bismuth subnitrate has the composition $BiNO_4+H_2O$, would correspond to 5.3842 grains of the latter. In the liver only an unweighable trace of bismuth was present.

A backward glance at the data already given enables us to see that the distribution of the arsenic is such as could result only from a case of chronic poisoning. The small but still weighable quantity found in the bones, and the regular distribution of the arsenic through all parts of the muscular tissue, are ample evidence of this fact. It is perhaps worthy of notice that the 55½ pounds of tissue contain more of the arsenic than all the internal organs. Many investigators have called attention to the absorption of arsenic by the muscle tissue, and the localization of arsenic in the muscles has long been accepted as a settled fact; but recently Scolosuboff,* under the guidance of Gautier, has attempted to show that arsenic, instead of localizing itself pre-eminently in the muscles, is specially absorbed and retained by the nerve tissue. The experiments upon which Scolosuboff based his conclusions were made upon animals poisoned with a solution of sodium arsenite, fed to them with their food; thus a bull-dog having taken during 34 days doses of As_2O_3 in the form of sodium arsenite, increasing from .005 gram to .150 gram per day, yielded the following results:

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* Bulletin de la Société Chimique de Paris, 24, 124.

100 grams fresh muscle	.00025	gram metallic arsenic
" " liver	.00271	" " "
" " brain	.00885	" " "
" " marrow	.00933	" " "

Scolosuboff also states that the results are still more striking in cases of acute poisoning. Thus he found that by injecting .15 gram of sodium arsenite under the skin of a bull-dog weighing 11 kilograms, death was induced in 17 hours; and while the arsenical mirror from the brain was very strong, it was less from the marrow, and scarcely visible from the liver and muscle. In another experiment, a griffin dog of the same weight received 10 grams of As_2O_3 in the form of arsenite, by injection into the cellular tissue. The animal died in 17½ hours. 100 grams of brain substance yielded a mirror of metallic arsenic weighing .00117 gram. The ring from 200 grams of liver, though plainly visible, was not weighable, while that from the muscles was almost invisible. Scolosuboff therefore draws the conclusion that arsenic is specially localized in the nerve tissue of the poisoned animal, and that in cases of acute poisoning the legal expert has need of searching for the metal specially in the brain of the victim; the liver, contrary to the usually accepted idea, when the action has been rapid, frequently not containing any of the poison. Such experiments as the foregoing, however, appear to our minds wholly valueless for toxical purposes, and the conclusion drawn from them very misleading. It is a well-known fact that the form of the poison modifies very decidedly the rapidity of its absorption, and it is quite probable that the form in which the poison is introduced may modify the rate and amount of absorption by different organs and tissues. And again, the period of time elapsing between the last dose of arsenic and the death of the animal, or, in other words, the length of time in which elimination has been going on since the last dose was given, may modify the results considerably, especially in the case of such a soluble combination as sodium arsenite, in which both absorption and elimination would naturally go on with rapidity. Cases of poisoning by solution of sodium arsenite are not of common occurrence compared with the number of those produced by the more insoluble white oxide, and deductions drawn from the experiments of Scolosuboff are not applicable to the common forms of arsenic poisoning, as is evidenced by the facts.

In the examination of the body of Mary Stannard,[*] where death was supposed to have taken place shortly after the introduction of the poison, one of us (J.) found 83.23 grains of arsenious oxide in the stomach, liver, and other internal organs, while the brain contained a hardly perceptible trace of arsenic; and in the examination of the body of Mrs. Riddle, 100 grams of abdominal muscle gave .00045 gram of metallic arsenic; 100 grams of muscle and ribs .0007 gram of metallic arsenic, and 100 grams of muscle from thigh .0004 gram of metal, while 300 grams of brain yielded an unweighable mirror.

An experiment conducted here in the laboratory on a large coach-dog gave the following results: 6.5 grams of solid As_2O_3 were given to the dog with meat during a period of 8 days in doses increasing from .1 gram to 2.5 grams per day. 24 hours after the last dose was given the dog was killed and examined.

100 grams of	intestines	gave	.0020	gram	metallic	arsenic
100 "	liver	"	.0010	"	"	"
113 "	kidneys	"	.0005	"	"	"
100 "	muscle	"	.0002	"	"	"
150 "	urine in bladder	"	.0003	"	"	"
Entire brain		"	faint mirror		"	"
100 grams of blood		"	distinct mirror		"	"

Thus it appears that in this case, as in the toxical cases quoted above, the amount of arsenic absorbed by the brain matter is very small compared with the amount absorbed by other tissues. In a very recent article on the distribution of arsenic in the animal body after the taking of arsenious oxide, E. Ludwig[†] finds by constantly agreeing results, that in the case of human beings as well as dogs poisoned by arsenic, both in acute and chronic cases, the liver contains the most arsenic; in acute forms the kidneys contain an abundant quantity; while the bones and brain, in either case, contain only a very small trace.

NEW HAVEN, *October* 4, 1880.

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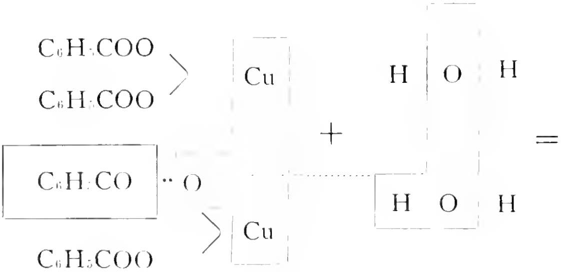
[*] Murdered, after administration of arsenic, by severing the blood-vessels of the neck, September, 1878.

[†] Anzeiger der K. Akad. d. Wissensch. Wien, No. 18, p. 18; also abstract in Jahresbericht Thier Chemie für 1879, p. 85.

SYNTHESIS OF SALICYLIC ACID.

BY EDGAR F. SMITH.

Upon heating 1 part of copper benzoate with about 3 parts of distilled water in a sealed tube at a temperature of 180° C., for a period of three hours, a large quantity of cuprous oxide separated. The contents of the tube were then removed to a rather large beaker, acidulated with hydrochloric acid, and the solution supersaturated with hydrogen sulphide. The filtrate from the copper sulphide contained, of course, a considerable amount of benzoic acid, which was removed by distillation in a current of steam. The residual liquid reduced to a small volume gave a crystallization of needles, fusing constant at 156° C., and afforded with ferric chloride the characteristic coloration given by salicylic acid. The salts also proved the presence of the latter. The reaction, then, described above may be graphically represented as follows:



$$Cu_2O + 3C_6H_5.COOH + C_6H_4OH.COOH.$$

Salicylic Acid.

The experiment repeated gave the same result A quantity sufficient for analysis was obtained, although its separation from the benzoic acid was attended with difficulty. In one or two instances the method was slightly modified. An aqueous solution of benzoic acid and an ammoniacal solution of cupric oxide were employed. The mixture was heated as usual, but it was necessary to increase the temperature to 220° C. The yield of salicylic acid in either case was never very abundant

LABORATORY OF UNIVERSITY OF PENNSYLVANIA.

REVIEWS AND REPORTS.

RECENT PROGRESS IN AGRICULTURAL SCIENCE.

The objects of agriculture may be briefly summarized as the production of certain plants and animals useful to man. It is the office of agricultural science to investigate and expound the chemical, physical and biological laws upon which this production depends, while the art of agriculture consists in the application in practice of the principles revealed by the study of the science. Corresponding to the two objects of agriculture just mentioned, we may logically consider agricultural science under the two heads of Vegetable Production and Animal Production, taking up under each one, first, the laws of vegetable or animal production in general, and second, the conditions under which such production is actually carried on.

VEGETABLE PRODUCTION.

Physiology and Bio-chemistry of the Plant.

GERMINATION.—The first act in the life of the plant is the germination of the seed from which it grows. The chemical changes taking place during this process are so similar to those which are continually going on in the mature plant that they may be conveniently considered in that connection, while here we take up briefly some of the recent contributions to our knowledge of the *conditions of germination.* These conditions are, in general, a proper temperature and the presence of sufficient moisture and oxygen.

Effect of Temperature on the Vitality and Germination of Seeds.—Numerous observations on these points have been made within a few years, with the purpose of ascertaining the limits of temperature within which germination is possible, and also within which seeds can retain their vitality.

The observations on the former point have been, in general, confirmatory of those of Sachs, though the minimum temperature at which germination can take place seems to be somewhat lower than is stated by that observer.

Thus Uloth* observed plants of wheat and of a species of maple, the seeds of which had been introduced into an ice-cellar along with the ice and had there germinated, and developed plants whose roots had penetrated the ice to a distance of, in some cases, over 16 cm. The germination must have taken place at a temperature little, if any, above 0° C., and as no cracks were observed in the

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* Jahresber. Agr. Chem. 13-15, 11, 99.

ice, it would seem that the heat developed by the chemical changes going on in the seedlings was sufficient to enable the roots to *melt* their way through the ice.

Kerner* experimented on the seeds of alpine plants, placing them in soil contained in glass tubes which were sunk in the water of certain cold springs whose temperature was practically constant at +2° C., and found them capable of germination under these circumstances. Kerner also states that many alpine plants not only germinate but grow and blossom under the snow and ice, penetrating the latter in the same manner as the roots of the wheat and maple observed by Uloth.

Haberlandt,† in some earlier experiments, found the minimum temperature for the germination of most seeds to lie between 3.8° and 8.4° C. Uloth's observation led to experiments on the effect of a temperature of 0°C. in germination. The experiments were made in a specially constructed ice-chest, on a large variety of seeds, with results differing somewhat from those noticed by Uloth. It was found‡ that out of twenty-five kinds of seeds, including those of the most important agricultural plants, sixteen, among which may be mentioned wheat, barley, oats and buckwheat, did not germinate at all; four, viz., rye, hemp, vetches and peas, did not pass beyond the first stages of germination; while mustard, *Camelina sativa*, Swedish clover (*Trifolium hybridum*), red clover, and lucerne showed a decided growth of the radicle. Nearly all the seeds of rye, about half those of the lucerne, 14 per cent. of the hemp, 17 per cent. of the mustard, and 10 per cent. of the red clover germinated. Haberlandt believes that the seeds capable of germinating at such a low temperature would yield plants needing for their development a less amount of heat than those growing from seeds of the same kind not capable of thus germinating, and that it might be possible in this way to produce early ripening or hardy varieties.

The same author has experimented on the germination of the seeds of tropical plants,§ and has found, as was to be expected, that the minimum temperature for the germination of these seeds is considerably higher than for the seeds of plants inhabiting colder latitudes, ranging from 10° to 15° C. It is worthy of note in this connection that the maximum temperature for these seeds was not essentially higher than for many plants which have become naturalized in temperate latitudes, while the minimum temperature is in many cases considerably higher. Haberlandt considers it as highly probable that, as a rule, those plants which are most widely distributed north and south are able to germinate at the most diverse temperatures.

The maximum temperature at which germination takes place varies considerably with different species, being in some cases as low as 20° C and seldom rising above 40° C.

The *vitality* of seeds is retained through a range of temperature

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* Jahresber. Agr. Chem. 16-17, I, 259.

† Landw. Versuchs-Stationen, 17, 104.

‡ Wissenschaftlich-prakt. Untersuch., 1, 113.

§ Ibid. 1, 117.

much exceeding that within which germination is possible. Dry seeds appear to be capable of withstanding quite low temperatures, while if previously soaked in water they are much more sensitive, as has been shown by Haberlandt[*] and by Detmer.[†] Haberlandt exposed seeds to the temperatures of —10° C. and —24° C.; he found that the former temperature diminished the germinative power less than the latter, that dry seeds suffered less than soaked ones, that quick thawing produced less injury than slow, and that those seeds which contained much oil were best able to withstand cold. The same experimenter[‡] has observed a curious effect of cold on flax. Soaked seeds of flax were exposed to a temperature of —17.5° C., were then slowly thawed, and sown as usual. The resulting plants showed an abnormal length of stem as compared with plants grown from the unfrozen seed, exceeding them by 39-45 per cent. in this respect. No further experiments confirmatory of this remarkable result have yet been reported.

The highest temperature which seeds can bear without losing their vitality seems to depend largely on their state of dryness, though differences are observed between different species and different individuals of the same species. Thus Just[§] found that clover seeds were killed at a temperature of 75° C. in an atmosphere saturated with water, and even at 50° C. did not survive for 48 hours, while dry seeds withstood temperatures below 120° C., though they germinated more slowly afterwards.

So, too, Haberlandt[||] found that soaking seeds in water of 40° to 50° C. diminished or destroyed the vitality of most seeds, and that even 30° C. was very injurious to some seeds, while v. Höhnel[¶] found that most seeds endured a temperature of 110° C. for an hour, if they were sufficiently dry (3 per cent. or less of water).

The fact of seeds withstanding the action of boiling water for some time, which has frequently been observed, is attributed by Haberlandt to the resistance of the outer coats of the seed to the water, which is thus prevented from reaching the interior of the seeds.

The length of time during which seeds are exposed to a high temperature is also an important factor in determining the result. In general, the higher the temperature and the moister the seed or the surrounding air, the sooner is the vitality destroyed. In some later experiments Just[**] has found that the vitality of some seeds is impaired by the action of moist air at ordinary temperatures, and Haberlandt, in his last cited paper, states that the germinative power of oats and barley is diminished by soaking in water at ordinary temperatures. Other seeds suffer no perceptible injury by such treatment; but as the temperature to which they are exposed is raised they lose their germinative power more and more quickly, until a temperature is reached which destroys it at once, or as soon as the seed has time to become heated through.

[*] Jahresber. Agr Chem 16-17 I 263.

[†] Forschungen Agr. Phys. II, 69.

[‡] Landw Versuchs-Stationen, 21, 357.

[§] Jahresber Agr. Chem. 16-17, I, 258.

[||] Wiss. prakt. Untersuchungen, 2, 47.

[¶] Ibid 2, 77.

[**] Jahresber. Agr. Chem. N. F. 1, 224.

It would seem that all seeds lose their vitality after a certain unknown (and probably long) time, and that the action of heat and moisture is simply to accelerate the processes which in any case lead in time to the death of the seed. In accordance with this view, Just (*loc. cit.*) found that exposure of seeds to a heat insufficient to kill them produced much the same effects as long storing, the seed germinating more slowly and feebly, as is the case with old seed.

Presence of Oxygen.—The presence of oxygen, as is well known, is essential to germination, and recent experiments by Haberlandt* go to show that in some cases the oxygen which is inclosed in the seed itself is necessary to initiate the germination. This observer experimented on seeds out of which the air had been pumped (the seeds being placed under water in the exhausted receiver of an air pump), and found that while in most cases no decided effect was observable, seeds of the oat, beet and fiesole were either incapable of germination, or that a far smaller percentage of them germinated than was the case without this treatment.

A certain dilution of the oxygen is also necessary. Böhm† has found that seeds are not able to get beyond the first stages of germination in pure oxygen at the pressure of the atmosphere, but that diminishing the pressure to about 150 mm. of mercury, either by dilution with hydrogen or by attenuation by means of the air pump, enables the germination to progress normally.

Too great dilution of the oxygen appears to be equally fatal. Bert‡ found that diminishing the pressure of the air in which the seeds were placed retarded their germination, and that the latter ceased entirely at a pressure of from 4–10 cm. of mercury, though the seeds retained their vitality. He ascribes the result to the decreased supply of oxygen consequent on the diminished pressure. On the other hand, he found that a pressure of 2 or 3 atmospheres slightly accelerated the germination, but that one of 4–5 atmospheres hindered it and a higher pressure stopped it. This result he ascribes to the too great density of the oxygen.

Finally, Cossa§ has found that nitrous oxide cannot take the place of oxygen. He found that while the seeds of wheat and maize used by him germinated in two days in air or oxygen, no signs of germination were to be seen after twelve days in those placed in nitrous oxide.

H. P. Armsby.

A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali, with the Collateral Branches. By George Lunge, Ph. D., F. C. S., Professor of Technical Chemistry at the Federal Polytechnic School, Zurich, (formerly manager of the Tyne Alkali Works, South Shields.) Vols. I and II. Van Voorst, London, 1878 and 1880.

This book, of which the first two volumes have now appeared, well deserves notice as a good example of a first-class monograph

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* Wiss. prakt. Untersuchungen, 1, 104.

† Jahresber. Agr. Chem. 16–17, I., 258.

‡ Jahresber. Agr. Chem. 16–17, I, 260.

§ Landw. Versuchs-Stationen, 18, 60.

treatise in the field of chemical technology. It proposes to describe in full, for the student and for the manager of works, the great group of allied manufactures which includes the production of sulphuric and hydrochloric acids, sodium sulphate, carbonate and hydrate, chlorine, bleaching powder, and their minor associates. The plan is admirably carried out for sulphuric acid, for soda by the Leblanc process, and for all minor products immediately dependent upon these, in the portion of the work already published, and doubtless will be brought to a handsome conclusion in the third volume, announced as soon to appear, in which the other processes of soda manufacture, chloride of lime and potassium chlorate, are to be treated.

The general arrangement of the large mass of material at the disposal of the author is clear and logical—material drawn from ample study of the literature of the subject, from personal experience in the direction of the principal forms of manufacture described, and from visits to and correspondence with many analogous works in England and on the continent of Europe.

Historical sketches of the rise and progress of the industries in question are given at the beginning of the various divisions of the work, and these, although brief and condensed, are sufficient for the most part in view of the main purpose of the book.

Good judgment is shown in the proportionate space allotted to different processes and modifications of practice, and in the criticism of these, and statement of the balance of advantages and defects which they exhibit, a fair and impartial spirit is observable. This is well illustrated by the discussion of the salt-cake process of Hargreaves in contrast with the use of the improved forms of sulphate furnace employing sulphuric acid. In a few instances one may doubt whether full justice has been done to a particular invention, as in the case of Sprengel's water-spray jet for the oil of vitriol chambers, the advantage of which, in giving control over the working temperature, does not seem to be sufficiently recognized; but this bears with it no appearance of partisanship. It is noteworthy that differences of English and Continental practice, or of usage in different districts, receive equal attention, as, for instance, the supply to the vitriol chambers of nitric acid in liquid form or in the state of vapor from nitre pots, the concentration of sulphuric acid in platinum or in glass vessels, the condensation of hydrochloric acid in stoneware jars or in coke-towers, etc.

Due notice is taken of improvements or variations of practice proposed, but not brought into use, while space is not wasted by over-lengthy discussions of methods incapable of being or very unlikely to be made of any real use. More attention is given to the progress already made with partially successful improvements, such as the utilization for the manufacture of sulphuric acid of sulphur dioxide from roasting of blende, copper and lead mattes, etc., than to desiderata still remaining to be supplied. Under this latter head it would seem that good results might be looked for from systematic research on the alloys of lead, with a view to diminishing the corrosion of the surface of the vitriol chambers; the value in this direction of a little antimony in the lead seems to be established, but whether the addition of some determinate amount of this alloy, or the use of some other metal with it or instead of it, might not give much better results seems worthy of further examination.

The general course of processes actually in use on the large scale is fully and clearly described, including of course all the more recently developed methods, such as the working of the Glover tower, (the importance of which in de-nitrating and concentrating sulphuric acid is strongly urged), the Hargreaves and Robinson process for making salt-cake by the direct use of sulphur dioxide from the burners, Mactear's mode of introducing surplus lime in the black-ball furnace, with the modifications subsequently made by Pechiney and Weldon, the production of caustic soda from tank-liquor, the improved form of Schaffner and Helbig's process for the recovery of sulphur from tank-waste, etc. The minute points of practical detail which so often distinguish a mere project or suggestion from a workable process are dwelt upon with due emphasis, and much useful experience is embodied in the comparison of practice at different factories. No allusion is to be found to the curious belief or superstition, whichever it may be, prevailing widely, it is said, among makers of sulphuric acid in this country, to the effect that Sicilian sulphur imported in old petroleum barrels, or as some claim, even in ships which have previously had a cargo of petroleum, burns with difficulty, requiring constant raking to keep it on fire, or a covering of sand on the burner to retain the heat. Even those who disclaim a belief in the alleged effect are in the habit of inserting a clause in their ship-charters against contact with petroleum.

Minor processes, not in general use, but employed at some works only, are not neglected, such as the purification of sulphuric acid by removal of arsenic, the industrial production of sulphur trioxide, and the like.

Mechanical and constructive appliances of all kinds, old and new, are described, and their several merits and defects considered; thus suitable space is devoted to the more recent forms of burners for pyrites in dust or small fragments, such as those of Hasenclever, Gerstenhöfer, Malétra and Schaffner; to various forms of acid pumps; to Faure and Kessler's stills of combined lead and platinum, and the newer forms of simple platinum stills for sulphuric acid concentration; to mechanical salt-cake furnaces, and to black-ash furnaces with revolving hearths.

Separate chapters are occupied with the theory of the more important and complex processes, and our present knowledge of the gaseous reactions occurring in the oil of vitriol chambers, of the changes brought about in the black-ash furnace, etc., is fairly presented. It is to be noted that Witt* has recently endeavored to

* Chemisches Central-Blatt, 14 April, 1880, S. 226.

show that nitrogen trioxide, N_2O_3, which Lunge assumes to be the oxide of nitrogen most largely present in the atmosphere of a normally working lead chamber, does not exist as such in the gaseous state, but splits at the moment of its production into a mixture of the dioxide and tetroxide. In evidence of this, Witt states that N_2O_4, which he views as nitrosyl nitrate, if conducted into a carefully dried solution of aniline in benzole, gives rise to the production of diazobenzol nitrate, and that if N_2O_3 be similarly treated, the same diazobenzol salt is formed and colorless NO is given off.

The methods of analysis applicable to the technical examination of the various materials used and products obtained are noticed, and various simple forms of apparatus for gaseous and liquid volumetric work are described. Results of the author's own experiments are occasionally given.

Sufficiently full accounts are given of the means of working up and utilizing by-products, as, for instance, the extraction of copper and silver from burnt pyrites.

Estimates of the cost of the more important processes are presented, and full estimates of the cost of plant are promised for the concluding volume. Under the head of yield obtained from given quantities of material, it is estimated that a very good average result of the Leblanc soda process in British alkali works will not show more than about 85.5 per cent. of the amount of product indicated by theory. In connection with one of the minor elements of cost in vitriol making, namely the loss of platinum dissolved by the acid from the stills, the statement is repeated which has appeared for the last few years, that this loss occurs with sulphuric acid quite free from the oxides or acids of nitrogen; but Scheurer-Kestner, the original authority on this subject, who has probably given to it more attention than any one else, has lately* claimed that perfectly pure sulphuric acid does not attack platinum, while extremely minute traces of the nitrogen compounds, easily overlooked in the application of ordinary tests, render it capable of dissolving quite considerable amounts of the metal. There are also some statistics of the supplies of raw material, and of production, but this division of the subject can hardly be said to exhibit equal scope and fulness of detail with the rest.

The illustrations are generally very good, the drawings large enough to be clearly intelligible, and for the most part to scale, with detail enough to serve as working drawings, while the engraver's work is very fairly done. The lettering of some of the figures is not very clear, which is always trying to the eyes in attempting to follow a description.

There are sundry useful tables, as of the indications of different hydrometers, the densities of acids, soda solutions, etc. A general index is promised to appear with the final volume of the work.

The annoyance of typographical errors has been avoided as far

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* Comptes rendus, 91; 59, 62

probably as can ever be expected in a book of so much extent and detail. Here and there a little slip of this sort may be noticed, as on p. 51 of Vol. 2, 5th line from bottom, where the word "material" should read "immaterial" The author's command of English is such as to make his pages pleasant reading, but odd turns of expression occasionally appear. Thus, in Vol. 1, on p. 38, we read of "*a furthergoing decomposition*"; on p. 39, that "*in the hot even zinc and iron already yield sulphurous acid*"; on p. 52, that "*probably the most sensitive of all reagents on nitric acid, etc., is,*" and on p. 141, that "*Petrie's burner . . . . is intended to permit a totally equal combustion of the sulphur.*" The sin of German-like *over*-fullness is not often committed in this book, but traces of it are not altogether wanting. Such a statement as appears at the top of p. 18, Vol. 1, to the effect that "*even in the animal kingdom free sulphuric acid has been found, viz: in the salivary glands of several mollusks, especially of Dolium galea, which contain 2.47 per cent. free sulphuric acid, and 0.4 per cent. of free hydrochloric acid.* (*Boedeker and Troschel; De Luca and Panceri,*") might surely have been omitted from a technological treatise. It is but an ungracious task however to look up such trifling blemishes as may exist in so good and able a book as the one under review; its general design and the general style in which that design has been carried out are deserving of hearty and ungrudging praise.

In laying down this work one cannot but feel regret that in the United States the manufacture of sulphuric acid has as yet attained but very moderate development, while the great industry of soda production, of so much importance in itself to the future of the nation, and involving so much of indirect consequence to the expansion of the other chemical arts, is represented by but the single factory at Natrona, employing as material the cryolite of the ice-bound Greenland coast.

J. W. M.

HANDBUCH DER ORGANISCHEN CHEMIE. Von Dr. F. BEILSTEIN, Professor der Chemie am technologischen Institute zu St. Petersburg. Erste Lieferung. Leipzig. Leopold Voss. 1880.

The idea of bringing together in one book *descriptions of every compound known to organic chemistry, with complete references to the literature of the vast subject*, is appalling. No one but a man of indomitable will and almost superhuman industry could ever seriously think of undertaking such a piece of work. Yet it has actually been accomplished by the author of the latest production in the field of organic chemistry which is described in the above title. In their time the classical works of Gerhardt and Gmelin were practically perfect, and these authors had in view exactly what Beilstein has; but these works have long since failed to furnish chemists with a satisfactory guide to the literature of organic chemistry, and, despite the large dictionaries of chemistry and the large text-books which have appeared within the last ten years, a want has been felt for some book which should be exhaustive, as far as references to literature are concerned, and at the same time should be brought down to date. At last the desired book is begun, and, judging by an examination of the first number and by the author's well-known reputation for thoroughness, we have no hesitation in saying that it will be all he promises and all we can wish for.

Unfortunately the beginning of a book in Germany is by no means a guarantee that it will ever be finished. Witness the great treatise on organic chemistry by Kekulé, for instance, whose incomplete third volume has been lying in many a library for thirteeen years. And in seeing this first number of a German book which must necessarily be very large, our first impulse is to assume that we shall never see the end of it, or, at least, that by the time the end is reached the beginning will be gray with the dust of ages. We are hence happy to say that the publisher promises, on the basis of manuscript already on hand, to finish the "Handbuch der organischen Chemie" in but little more than a year. There are to be about twelve numbers of 160 pages each, and these will appear at intervals of from five to six weeks uninterruptedly until the work is completed. This will make about 2000 pages, but they are large pages and printed in small type, so that the material presented would cover at least 4000 ordinary octavo pages.

The price of the book is remarkably low, bringing it within the reach of every one who needs it. Each number costs but three marks (about 75 cts.), thus making the price of the complete work only from $9.00 to $10.00.

The time for criticizing this work has not arrived, nor is it possible for one man to subject it to criticism from the only legitimate standpoint. The main question to be answered is whether the book is what its author claims it to be. Is it exhaustive? This can only be answered in the future by special investigators who have had occasion to use it as a book of reference. We have every reason to believe, however, that it will be found a thoroughly trustworthy guide to the original sources, and, as such, it will be of incalculable value to the earnest student and investigator. I. R.

SOME RECENT INVESTIGATIONS IN PHYSICAL CHEMISTY.

Within the last few months there have appeared in the chemical journals some articles in the field of physical chemistry of much more than ordinary interest and importance The first of these to which we would call attention is by JULIUS THOMSEN. It is entitled "*Thermochemical Investigations on the Theory of Carbon Compounds.*"* Thomsen first gives the figures obtained by him for the heats of combustion of marsh gas, CH_4, ethane, C_2H_6, pro-

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* Ber. d. deutsch. chem. Gesell. 13, 1321.

pane, C_3H_8, ethylene, C_2H_4, propylene, C_3H_6, and acetylene, C_2H_2. From these experimental data he calculates by well-known methods the heats of formation of these compounds.

The results are given in the table below:

Hydrocarbon.	Molecule.	Heat of Formation.
Methane	CH_4	19570 c
Ethane	C_2H_6	24510 c
Propane	C_3H_8	29950 c
Ethylene	C_2H_4	— 4740 c
Propylene	C_3H_6	— 400 c
Acetylene	C_2H_2	—48290 c

From these figures we see how much heat is developed: (1) when two atoms of hydrogen combine with two atoms of carbon; (2) when four; (3) when six; and (4) when eight atoms of hydrogen combine with two atoms of carbon. We have:

		Difference.
C_2+H_2	—48290 c	550 c
C_2+H_4	— 4740 c	29259 c
C_2+H_6	+24510 c	14630 c
C_2+H_8	+39140 c	

The differences, it will be observed, are multiples of a constant, about 14600, and stand in the relation 3 : 2 : 1. If the regularity here observed be of general application, then we can complete the above table by the member C≡C, and the heat of formation of such a molecule of gaseous carbon would be —106630 c. Calling this value a, we have:

Compound to be formed.	Heat of Formation.	Diff.
$C\equiv C$	$-a$	$4r$
$HC\equiv CH$	$-a+4r$	$3r$
$H_2C=CH_2$	$-a+7r$	$2r$
H_3C-CH_3	$-a+9r$	r
$H_4C\vdots CH_4$	$-a+10r$	

The most probable values for the two constants a and r are

$$a=106630\text{ c.}\quad r=14573\text{ c.}$$

The gasification heat of carbon, *i. e.* that quantity of heat which is necessary to transform two atoms of amorphous carbon into the normal gaseous condition and to form the molecule C≡C, amounts to 106630 c.

The signification of the constant r requires further examination. We may regard the gasification heat of carbon as made up of two factors: (1) the heat of dissociation of two atoms of carbon, *i. e.* that quantity of heat which is necessary to put two atoms of amorphous carbon in the gaseous condition *as separated atoms*; (2) the heat tonality which results when two such atoms unite by means of four bonds to form a molecule of normal gaseous carbon. Let us call the first quantity $2d$, the latter C≡C or v_4, then we have

$$-a = -2d + v_4 = -106630 \text{ c.}$$

Further, when the separated carbon atoms unite with hydrogen, three processes are to be distinguished: (1) the hydrogen molecule is dissociated by the use of an amount of heat which we may designate by $-hh$; (2) these free hydrogen atoms unite with carbon with an evolution of heat $2ch$; (3) the carbon atoms unite with each other by one, two or three bonds; the single, double and triple union may be designated by v_1, v_2 and v_3.

The formation of acetylene may be represented thus:

$$\mathrm{HC{\equiv}CH} = (\mathrm{C_2,H_2}) = -2d + v_3 + 2ch - hh.$$

Assuming that, whenever hydrogen unites with carbon to form hydrocarbons, the same heat tonality results from equal numbers of atoms, and making $2ch - hh = 2q$, we have:

$$\begin{array}{llcl}
\mathrm{C{\equiv}C} & -a & = & -2d + v_4 \\
\mathrm{HC{\equiv}CH} & -a + 4r & = & -2d + v_3 + 2q \\
\mathrm{H_2C{=}CH_2} & -a + 7r & = & -2d + v_2 + 4q \\
\mathrm{H_3C{-}CH_3} & -a + 9r & = & -2d + v_1 + 6q \\
\mathrm{H_4C : CH_4} & -a + 10r & = & -2d + \ldots + 8q
\end{array}$$

and subtracting each succeeding equation from the preceding we have further:

$$\begin{array}{lcl}
v_4 - v_3 & = & 2q - 4r \\
v_3 - v_2 & = & 2q - 3r \\
v_2 - v_1 & = & 2q - 2r \\
v_1 & = & 2q - r.
\end{array}$$

These equations indicate the possibility of determining the values of v_4, v_3, v_2 and v_1, but other determinations are necessary before these equations can be solved.

The heats of combustion of carbon and its two oxides (C,O), (CO,O) and ($\mathrm{C,O_2}$) are known, the last two being determined directly, and the first one being the difference between them. The values found by Thomsen are included in the subjoined table:

Reaction.	Heat evolved.
(C,O)	28880 c
(CO,O)	68080 c
($\mathrm{C,O_2}$)	96960 c

Now, operating as above with the hydrocarbons, let $-2d$ represent the heat of dissociation of a molecule of carbon; $-oo$ the heat of dissociation of a molecule of oxygen; co the heat of combination of one atom of carbon and one atom of oxygen; and oco the heat of combination of one atom of carbon with two atoms of oxygen; then we have

$$\begin{aligned} 2(C,O) &= -2d-oo+2co, \\ (C,O_2) &= -\ d-oo+oco, \end{aligned}$$

and subtracting one equation from the other,

$$(C,O_2)-2(C,O)=d-2co+oco=39200\ \mathrm{c}.$$

If the same amount of heat is evolved when two atoms of oxygen unite with two separate carbon atoms, and when they unite with one carbon atom, or, if $2co=oco$, then $-2co+oco=0$, and it follows that $d=39200$ c. But it may be that $2co$ is not equal to oco, then we should have $d=39200\ \mathrm{c}+x$.

From the values thus deduced for a, r and d, the equation

$$2(C,H_4) = -2d+8q = -a+10r$$

gives

$$q=14687\mathrm{c}+\frac{x}{4}.$$

But $q=ch-\frac{hh}{2}$, according to the above, hence

$$ch=14687\mathrm{c}+\frac{hh}{2}+\frac{x}{4}.$$

Now turning again to the equations given above, viz.:

$$\begin{array}{lccccl} C\underline{\equiv}C & -a & & & = -106630\ \mathrm{c} & = -2d+v_4 \\ HC\equiv CH & -a & + & 4r & = -\ \ 48338\ \mathrm{c} & = -2d+v_3+2q \\ H_2C=CH_2 & -a & + & 7r & = -\ \ \ \ 4619\ \mathrm{c} & = -2d+v_2+4q \\ H_3C-CH_3 & -a & + & 9r & = +\ \ 24527\ \mathrm{c} & = -2d+v_1+6q \\ H_4C : CH_4 & -a & + & 10r & = +\ \ 39100\ \mathrm{c} & = -2d\qquad +8q \end{array}$$

and inserting for d and q the values just obtained, we have

$$\begin{aligned} v_4=c\underline{\equiv}c &= -28230\mathrm{c}+2x \\ v_3=c\equiv c &= +\ \ \ 688\mathrm{c}+\tfrac{3}{2}x \\ v_2=c=c &= +15033\mathrm{c}+\ x \\ v_1=c-c &= +14805\mathrm{c}+\tfrac{1}{2}x. \end{aligned}$$

The values found for q, r and ch are then

$$\begin{aligned} q&=14687\mathrm{c}+\frac{x}{4} \\ r&=14570\mathrm{c} \\ ch&=14687\mathrm{c}+\frac{hh}{2}+\frac{x}{4}. \end{aligned}$$

On examining the values for v_4, v_3, v_2 and v_1 the same constant is seen to play a part in these as in the values for q, ch and r. The constant is practically identical with r, from which follow the expressions,

$$
\begin{aligned}
q &= \quad r+\frac{x}{4} \\
v_1 &= \quad r+\frac{x}{2} \\
v_2 &= \quad r+x \\
v_3 &= \quad o+\tfrac{3}{2}x \\
v_4 &= -2r+2x
\end{aligned}
$$

The most probable value for d is 39200 c$+x$. With the results thus far reached it is possible to calculate the heat of formation of any hydrocarbon $C_n H_{2m}$. The general formula is

$$(C_n\,,\, H_{2m}) = -\,nd+2mq+\Sigma v,$$

in which Σv is the sum of the values for v_3, v_2, and v_1, which occur in the compound. A table is then given in which it is shown that the calculated and found values for the heat of formation of the hydrocarbons thus far experimented upon agree very closely. If the accuracy of the general formulas be conceded, then we have a new method in our possession for determining the constitution of hydrocarbons, a method, however, which is only applicable for the purpose of distinguishing between cases in which double or triple union of carbon atoms may occur.

To illustrate the application of the method, the case of benzene, C_6H_6, may be cited. If Kekulé's formula for this body is correct, its heat of formation, according to Thomsen's principle, should be

$$-6d+6q+3v_1+3v_2 = -60360 \text{ c.}$$

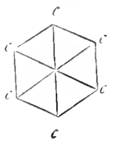
If there were no double union in benzene the heat of formation should be

$$-6d+6q+9v_1 = -16650 \text{ c.}$$

These values for the heat of formation correspond to the following values for the heat of combustion:

For 3 single and 3 double unions,	846040 c.
For 9 single unions,	802330 c.

The heat of combustion found by Thomsen* for benzene is 805800 c, hence he concludes that Kekulé's formula is not correct. The simplest formula which can be devised for benzene on the basis of nine single unions between carbon atoms is that in which each carbon atom is united with three others as represented thus:



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* Ber. d. deutsch. chem. Gesell. 13, 1806.

A second investigation of importance is by J. W. **Brühl**, entitled "*The Chemical Constitution of Organic Bodies in Relation to their Density and their Power to Transmit Light.*"* This investigation was carried out in the laboratory which is under the direction of Prof. H. Landolt, and is characterized by great fullness and evidences of accuracy. A great many liquids have been examined by the author with reference to their refracting power, and he has succeeded in establishing important relations between this power and the constitution of the bodies.

In order to have results that can be compared with one another, the *refraction-equivalent* is determined. This is represented by the expression $P(\frac{n-1}{d})$, in which P is the molecular weight, n the index of refraction, and d the density of the body. The index is determined for four different lines of the spectrum obtained from the sodium light and from the light emitted by hydrogen in a Geissler's tube. As regards the interesting and important details of the paper, reference must be made to the original, which will well repay careful study. Here only the main results of the investigation will be summed up as briefly as possible.

Landolt has shown that, in general, bodies of the same composition have the same refraction-equivalent, the value of this equivalent being dependent upon the number and kinds of atoms present in a molecule, rather than upon the arrangement of these atoms. Each atom must then have its own refraction-equivalent, and, if we know what this is, we can calculate the equivalent for any given compound. In order to determine these quantities for carbon, hydrogen and oxygen, Landolt adopted different methods, only one of which need here be referred to. Two compounds were compared with each other, the compositions of which differed by one atom of carbon, two atoms of hydrogen or one of oxygen, and the difference in the molecular refraction of the two bodies gave the refractive power of the elements.

	Difference in Composition C_1. $P(\frac{n-1}{d})$	Diff.
Methyl alcohol, CH_4O	13.17	5.41
Aldehyde, C_2H_4O	18.58	
	Difference in Composition H_2.	
Aldehyde, C_2H_4O	18.58	2.12
Ethyl Alcohol, C_2H_6O	20.70	
	Difference in Composition O_1.	
Aldehyde, C_2H_4O	18.58	2.53
Acetic Acid, $C_2H_4O_2$	21.11	

As the mean of a large number of experiments the following values were obtained for the atomic refraction of the three elements:

$$C=5;\ H=1.3;\ O=3.$$

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* Ann. der Chemie, 200, 139; 203, 1,255, 363.

By means of these figures, then, we can calculate the refraction-equivalent of any given body composed of these three elements. On comparing the calculated values with those determined by experiment, the two are indeed found to be equal in a large number of cases, but at the same time, it is evident, in a number of other cases, that the values found by experiment are greater than those calculated. More careful examination of the subject shows that all the bodies which form exceptions to the general rule belong to the class of unsaturated compounds; and that all saturated compounds give results in harmony with the rule.

With great precautions the author has subjected a large number of pure liquid organic compounds to investigation. He has determined especially the density and the indices of refraction, and from these obtained the refraction-equivalents. A study of the results shows that the increased molecular-refraction noticed in connection with unsaturated compounds is proportional to the number of double unions between carbon atoms found in the compounds. For one double union the molecular-refraction is increased by two, for two there is an increase of four, and for three an increase of six. The law is thus stated by the author:

The excess of the molecular-refraction of bodies over the value calculated from the chemical formula is proportional to the number of carbon double unions found in the body, and, when the number of these is z, the excess amounts to z.2.

$$M = P\left(\frac{n-1}{d}\right) = R + z.2.$$

In this formula M is the refraction-equivalent actually observed, and R is the calculated value.

This law represents the principal result of the investigation, though many other results of interest are discussed in the paper.

It is shown, for instance, that:

Univalent elements have a constant atomic refraction.

The results of the investigation enable us to determine the constitution of many organic substances. Illustrations are given of the application of the principle for this purpose. It is curious to note that Brühl proves the correctness of Kekulé's formula for benzene, while Thomsen proves its incorrectness, a paradoxical state of things which requires further examination.

In continuing his work Brühl has, further, shown that there is a difference between the atomic refraction of oxygen when it is combined as in carbonyl, $C=O$, and when it is combined as in hydroxyl, $C—O—H$, a result which is of value in connection with the determination of the structure of such compounds as contain oxygen.

Finally, the author discusses the general relations existing between the constitution and physical properties of bodies. It would lead too far to go into details in regard to this part of the paper, but a few statements may be made which will serve to give an idea of the subject-matter.

It is shown that *the boiling points, densities and indices of refraction vary in the same way; that for isomeric bodies the constants of that one are largest which consists of an uninterrupted chain of hydrocarbon residues, and that the constants become smaller the more the structure of the molecule is branched and deviates from one direction.*

The data thus far established seem also to show that the shorter the molecule of isomeric bodies, *i. e.* the more they approach the spherical form, the larger is the molecular volume.

The words "shorter," "branched," etc., used in the above statements have primarily, of course, reference to the appearance of the formulas in common use which are not supposed to represent the arrangement of the atoms in space But assuming that these formulas do in a crude way represent the actual shapes of the molecules, it is shown that there probably exists a direct connection between the variations in the physical constants of isomeric bodies and the actual shape of their molecules.

Thus the specific gravity of bodies with long molecules would necessarily be greater than that of bodies with branched or spherical molecules, for the same reason that we can get more rods in a given space than spheres of the same weight.

So also with reference to the boiling point. The rod-shaped molecules offer the most points of contact, the spherical the least. The adhesion between molecules of the first kind will hence be the greatest, and the passage of the body into the form of vapor will be more difficult than is the case with other bodies, or the boiling point will be higher. Similar considerations indicate that the facts observed in connection with the time of transpiration of vapors are in harmony with the view that the usual formulas actually represent the shapes of molecules.

Two further papers have appeared, the results of which are of importance to the subject treated in Brühl's memoir. These are: 1st. "*On the relation between the molecular weights of substances and their specific gravities when in the liquid state,*" by T. E. Thorpe;* and 2d. "*On the time of transpiration of vapors,*" by R. Pribram and A. Handl.† Space will not permit, however, more than a simple reference to these papers. They both appear to be models of accurate investigation and both have led to important results. They are to be continued, and we may look for further developments of interest. The amount of painstaking labor involved in all the investigations here referred to is enormous, and the authors certainly deserve great credit for the work they have done.

I. R.

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* Journal of the Chemical Society (London), 1880, pp. 141, 189, 327, 341.

† Sitzungsberichte der Wiener Akad. der Wissensch. 80, 17.

THE ATOMIC THEORY. By Ad. Wurtz, Membre de l'Institut; Doyen Honoraire de la Faculté de Médecine; Professeur à la Faculté des Sciences de Paris. Translated by E. Cleminshaw, M. A., F. C. S., F. I. C., Assistant-Master at Sherborne School. C. Kegan Paul & Co., 1 Paternoster Square, London. 1880.

It is a peculiar fact that in France, which is frequently claimed as the birth-place of chemistry, and where many of the important advances which have led to the development of what is called "modern chemistry" have undoubtedly been made, there should exist to-day a strong feeling among a class of prominent chemists in opposition to the very foundation of modern chemistry, the atomic theory. It is to this fact perhaps that we owe, at least partially, the book which forms the subject of this notice. The writer of the book, M. Wurtz, has taken upon himself the championship of the atomic theory in opposition to the severe censures of the conservative school which is headed by Berthelot and St. Claire-Deville, and for some time past an interesting discussion has been carried on in the pages of French scientific journals, in which the above-named chemists have taken most prominent part.

The book before us may be regarded as a summing up of the case for the atomic theory. As it is written ostensibly for popular reading, it deals as little with purely technical matters as the nature of the subject will permit, though we doubt whether any one but a chemist fairly well trained in his subject could read it understandingly. In general it is clear and logical, and its study will be of benefit to the earnest student of chemical philosophy. It is true that the author here and there gives evidences of his position as advocate in the case, and allows his feeling of partisanship to show itself. In the first part of the book, which has to deal with the earlier stages of the historical development of the subject, this is not so noticeable, but in the chapters upon Atomicity, Affinity and the Constitution of Bodies it is certainly a defect.

The work is divided into two parts, Book I treating of Atoms, and Book II of Atomicity.

There is scarcely anything to be said save in commendation of the first part of the book. It contains very little that is new, and, in the estimate which the writer places upon the value of the investigations discussed, he agrees with most others who have treated the subject, as Kopp, Ladenburg and Lothar Meyer. A full and clear exposition of the views of Mendelejeff is given and the *periodic law* is enthusiastically spoken of. As regards this part of the subject, a serious disagreement has arisen between Lothar Meyer and Wurtz, the former claiming that sufficient credit has not been given him in connection with the relations between the atomic weights and the properties of the elements. Public letters on the subject have been exchanged, and finally Mendelejeff has expressed himself in no ambiguous terms in reply to Meyer. The discussion is still open and at present stands about in this way: Wurtz gives Mendelejeff almost the entire credit for the discovery of the great periodic law, and Mendelejeff agrees with Wurtz in his view of the subject. Lothar Meyer, on the other hand, regards himself as the real discoverer of the law, or rather as one whose labors have done a great deal to perfect it.

Special attention is called to the relation which exists between the atomic weights and the power of bodies of emitting luminous rays, as described by Lecoq de Boisbaudran. This chemist "has proved that, for analogous elements, such as potassium, rubidium and cæsium; calcium, strontium and barium; aluminium, gallium and indium, the increase of atomic weight is proportional to the increase of wave-length, which corresponds with the spectral lines of each of these metals."

In treating of atomicity the author has hardly succeeded in throwing new light upon this intricate subject. He first shows how the present view regarding the property of atomicity had its origin in the early recognition of "the unequal saturating capacity possessed by bases for acids, and the unequal saturating capacity possessed by acids for bases;" how from this origin came the distinction between radicals of different basicity and the idea of types. Then came the researches of Frankland on organo-metallic bodies, and in a paper published in 1852 (not 1872 as is erroneously stated) this chemist first "called attention to the power which metals possess of combining with a fixed and definite number of atoms."

The development of the idea of atomicity is clearly set forth, indeed we do not recall a better treatise on this subject. But coming down to the present, the author is of course brought face to face with the same difficulties which other writers have encountered, and we think he has not been more successful than others in overcoming them. That there is a property of atoms, or of matter, which is somewhat vaguely designated by the term atomicity, very few will be inclined to doubt, but when it comes to giving a definition of this property, the accurate thinker must necessarily, in the present state of our knowledge, be puzzled. There are serious objections to considering atomicity as a fixed property, and there are also some objections to the opposite view, viz., that it is a variable property. M. Wurtz wisely adopts an intermediate course, stating that atomicity is a relative property of atoms, *i. e.* the atomicity of any given atom is determined, to some extent, by the nature of the atom or atoms with which it enters into combination. There is undoubtedly a germ of truth in this view of the matter, but it does not end the difficulties; for, even granting that any given element is trivalent towards one element and quinquivalent towards a second, it cannot be claimed that these relations are fixed. Take the case of phosphorus for example. This element is said to be trivalent towards hydrogen and quinquivalent towards chlorine. But we know that phosphorus also acts as a trivalent element towards chlorine, as is clearly shown in the compound PCl_3. If, then, phosphorus may act as trivalent and quinquivalent towards chlorine, why may there not be conditions under which it may act as quinquivalent towards hydrogen? And then what basis is there for the statement that phosphorus is trivalent towards hydrogen and quinquivalent towards chlorine? A similar line of thought applied in other cases shows that this idea of relative atomicity, attractive as it may at first appear, really helps us very little, if any, in a thorough comprehension of the general nature of atomicity, and it certainly does not enable us to give a clear and accurate definition of the property.

In the chapter on Constitution of Compounds the impression is left on the mind of the reader that the constitution of bodies is determined mainly by the aid of the idea of atomicity. It is true that the constitutional formulas now in use are based upon the mutual saturating power of atoms, but a formula which is not deduced from facts established by experiment, and which is simply constructed in such a way as to satisfy the hypothetical bonds of the atoms, is not of much value, and cannot be of much value, until our conceptions of atomicity are much clearer than they are at present. By way of illustrating the force of this remark, we may take the case of alcohol. The structural formula now used for this compound, viz., $C_2H_5—O—H$, is chiefly valuable as an expression of facts. It points out that one hydrogen atom in alcohol differs from the others, and that it is intimately associated, if not united directly, with the oxygen atom. These are facts, or at least they are the simplest interpretations of reactions actually observed. And we have a right to demand that every formula used shall, in a similar way, be an expression of facts established. By far too many of the formulas found in books are, however, simply the results of attempts to account for the atomicities of the atoms which form the constituents of the compounds represented. It is in the highest degree probable that the time will come when, given the conditions under which a compound exists, we shall be able to state with a considerable degree of certainty how the atoms are combined in the compound; but that time has not yet come, and before it comes the general nature of atomicity must necessarily be investigated much more thoroughly than it has yet been, and our ideas concerning it must become much more definite.

I. R.

NOTES.

The Opium Alkaloids.

The connection between the alkaloids from Peruvian bark and the pyridine bases has been established by a number of recent investigations, to which special attention has been called in former numbers of this Journal. E. v. GERICHTEN has now shown that a similar connection probably exists between the opium alkaloids and the pyridine bases. Apophyllenic acid, a substance obtained by oxidation indirectly from narcotine and directly from cotarnine, is shown to be the methyl ester of pyridinedicarbonic acid, $C_5H_3N(CO_2H)_2$. When apophyllenic acid is heated with concentrated hydrochloric acid to a high temperature, methyl is extracted and pyridinedicarbonic acid is produced. The latter yields pyridine C_5H_5N when heated with soda-lime.—(*Ber. d. deutsch. chem. Gesell.*, 13, 1635.)

River Water.

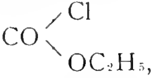
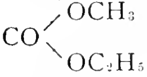
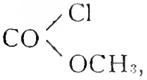
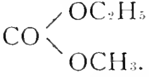
As the result of an elaborate investigation, C. M. TIDY has reached the following conclusions:

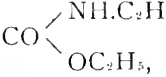
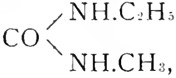
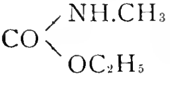
1. That when sewage is discharged into running water, provided the primary dilution of the sewage with pure water be sufficient, after the run of a few miles, the precise distance of travel being dependent on several conditions, the removal of the whole of the organic impurity will be effected.

2. That whatever may be the actual cause of certain diseases, *i. e.* whether germs or chemical poisons, the *materies morbi* which finds its way into the river at the sewage outfall is destroyed, together with the organic impurity, after a certain flow.

E. FRANKLAND takes exception to Tidy's conclusions, reviewing the evidence on both sides very carefully, and showing that the oxidation of sewage contained in river water cannot and does not take place rapidly. He concludes, hence, that the question, "Can running water be at all times safely used for dietetic purposes a few hours or days after it has been mixed with sewage?" must be answered in the negative. The introductory paragraph of Frankland's paper is here given:—"Twelve years ago there was a general impression amongst chemists and others that polluted water quickly regained its original purity by spontaneous oxidation. This opinion had no foundation in quantitative observations; indeed, there was not a single experimental fact to support it, for the previous condition of water analysis did not permit of the quantitative investigation of organic matter dissolved in water. The impression had gained currency from the improved appearance of a polluted river after a flow of a few miles, and also from the disappearance of smell and blackness from putrescent water under similar circumstances. Two classes of persons, strongly interested in its acceptance, were chiefly instrumental in the origination and diffusion of this opinion. These were, first, polluters of running water; and, secondly, water companies drawing their supplies below the sewer outfalls of towns. Both these influential classes, with enormous interests at stake have always contended that even the most abominable of organic rubbish is destroyed by oxidation, in fact utterly 'burnt up,' during a flow of a few miles. There being no similarly organized opposition to the notion, the extensive credence which it gained from those who did not care much to investigate its truth, is not surprising. It was a comfortable doctrine, and therefore a popular one. Nevertheless it did not pass entirely unchallenged; indeed, it is difficult to imagine how any chemist, accustomed to the habits of organic compounds, could accept such an opinion without the most conclusive proofs of its correctness."—(*Jour. Chem. Soc.*, May and July, 1880.)

Two Remarkable Cases of Metamerism.

LUDWIG SCHREINER has just announced a discovery of the highest importance. He has shown that, when ethyl chlorocarbonate,  $\mathrm{CO}\Big\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{OC_2H_5}\end{matrix}$, is allowed to act upon a solution of sodium methylate $CH_3.ONa$, a compound is formed of the formula  $\mathrm{CO}\Big\langle\begin{matrix}\mathrm{OCH_3}\\ \mathrm{OC_2H_5}\end{matrix}$ which he calls *ethyl methylocarbonate*, the properties of which are well defined. If now methyl chlorocarbonate,  $\mathrm{CO}\Big\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{OCH_3}\end{matrix}$, be allowed to act upon sodium ethylate $C_2H_5.ONa$, a compound of the same empirical formula as that above mentioned is obtained, but the two differ markedly in their properties. This second product is called *methyl ethylocarbonate*, and its formula is  $\mathrm{CO}\Big\langle\begin{matrix}\mathrm{OC_2H_5}\\ \mathrm{OCH_3}\end{matrix}$. The first product has the specific gravity 1.0372 and boils at 104°, the second has the specific gravity 1.0016 and boils at 115.5°.

In a similar way the author has succeeded in preparing two methyl-ethyl-ureas. For this purpose the compound,  $\mathrm{CO}\Big\langle\begin{matrix}\mathrm{NH.C_2H_5}\\ \mathrm{OC_2H_5}\end{matrix}$, was treated with methylamine, and was thus converted into ethyl-methyl-urea,  $\mathrm{CO}\Big\langle\begin{matrix}\mathrm{NH.C_2H_5}\\ \mathrm{NH.CH_3}\end{matrix}$, a body fusing at 105°; and, on the other hand, by treating the body  $\mathrm{CO}\Big\langle\begin{matrix}\mathrm{NH.CH_3}\\ \mathrm{OC_2H_5}\end{matrix}$ with ethylamine the product has the same formula as the ethyl-methyl-urea first obtained, but it has not the same properties. It fuses at 75° and does not crystallize as well.

If the results obtained by Schreiner should be verified by continued investigation, it is difficult to see how the now commonly accepted idea of the equivalence of the four affinities of the carbon atom can be maintained.—(*Journal für prak. Chemie, N. F.* 22, 353.)

The Atomic Weight of Glucinum.

Nilson and Pettersson have recently determined the specific heat of glucinum at different temperatures and conclude from their experiments that its atomic weight should be changed to 13.65. If this is really the atomic weight of glucinum, then it is impossible to include it in the table of Mendelejeff, or, at least, the place to which it would be assigned in the table would not be in harmony with its properties. LOTHAR MEYER has now taken the results of Nilson and Pettersson and shown that their conclusion is not justified, that their results correctly interpreted lead to the confirmation of the commonly accepted atomic weight for glucinum, viz. 9.10.—(*Ber. d. deutsch. chem. Gesell.* 13, 1780.)

On the Nature of Caucasian Petroleum.

Recent investigations on the petroleum found in such enormous quantities in the Caucasus have shown that it has an illuminating power about 10 per cent. greater than American petroleum, and that, in spite of its higher specific gravity, it is drawn up by lamp wicks better than the American oils. F. BEILSTEIN and A. KURBATOW have undertaken a chemical examination of the more volatile portions of the crude petroleum, and have found that they consist mainly of the hydrogen addition-products of the aromatic hydrocarbons C_nH_{2n-6}. These hydrocarbons have been thoroughly investigated by Wreden. On comparing the substances from Caucasian petroleum with those described by Wreden the identity was established. The best known members of the series are: Hexahydrobenzene, C_6H_{12}; hexahydrotoluene, C_7H_{14}; and hexahydroxylene, C_8H_{16}.—(*Ber. d. deutsch. chem. Gesell.* 13, 1818.)

NOTE.—A complete list of publications relating to chemistry from the time of the last list to the present will be given in the next number.

ERRATUM.

The numeral VI. in connection with the title p. 305 should refer to the general title "On the Ethers of Uric Acid."

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CHEMICAL JOURNAL.

ON A SIMPLE FORM OF APPARATUS FOR DETERMINING THE SPECIFIC HEATS OF SOLIDS AND LIQUIDS WITH SMALL QUANTITIES OF MATERIAL.

BY J. W. MALLET, F. R. S.

Both of the most trustworthy forms of apparatus hitherto in use for the determination of specific heat—those of Regnault and Bunsen—are somewhat troublesome to prepare for an experiment, the latter notably so. Regnault's calorimeter requires a fresh measurement of the water for each occasion of use, and gives accurate results only with considerable quantities of the materials to be examined,* so that in the case of rare substances, of which but a few grams can be had, it ceases to be available. Bunsen's ice calorimeter, beautiful as the instrument is in principle, and capable of being applied to but a fraction of a gram of material, can be repeatedly used within a few hours, or at most days, after it has been packed in snow or shaved ice, but when longer set aside, demands, as has been said, no small care and trouble to get it again ready for use.

An arrangement which shall avoid these disadvantages, which shall be simple, and capable of immediate use after having stood

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*Several hundred grams were used in each of a large number of Regnault's own experiments.

aside for weeks or months, which shall work with but little of the material under examination, and which shall give results not necessarily equal in accuracy to the best that may be obtained by more elaborate methods, but accurate enough for the ordinary application to be made by the chemist of a knowledge of specific heat, as bearing on atomic or molecular weight, seems likely to be useful, and may serve to render approximate determinations of this physical constant more frequent, in something the same way that the apparatus of V. Meyer has facilitated the determination of vapor density.

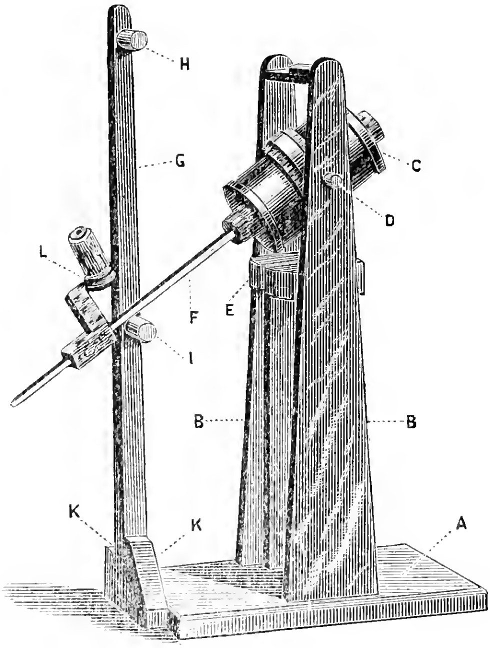

Fig. 1.

Fig. 1 shows in elevation the general appearance of a little calorimeter which I have found to fairly fulfil these conditions; the figure is from a photograph, and of about one-sixth the linear dimensions of the original. The base *A* and two uprights *B B* are made of hard wood. The cylindrical body *C* of the calorimeter is mounted upon two brass pins *D* passing through the opposite uprights, so that it can be turned round an axis at right angles to its axis of figure. A cross-piece of wood *E* serves to rest the fingers upon in grasping *C* at the time of use, and elastic bands of india-rubber are stretched across between the uprights to prevent the accidental breaking of the thermometer *F* by violent swinging round of *C*, from which it projects. An upright arm *G* bears upon it two corks *H I*, between which the thermometer moves, and the distance apart of these corks determines the extent of motion of rotation of *C* during use. The arm *G* itself turns on a pin screwed into the end of the base, so that it (*G*) can when necessary be turned back out of the way of the thermometer, which can then move further up or down. Two little blocks of wood *K K*, respectively in front of and behind the lower end of *G*, serve as stops to regulate the throwing it into position or back out of the way as required. A reading lens *L* is arranged upon a cork support to slide upon the stem of the thermometer at a proper distance from its scale, and error of parallax is avoided by a short tube above the lens with a small hole in the upper end to sight through.

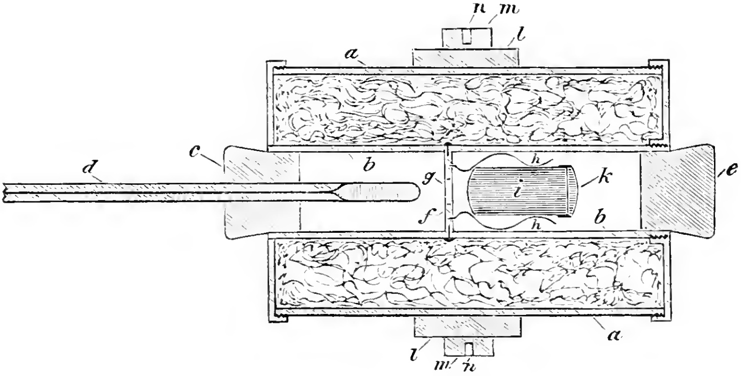

FIG. 2.

Fig. 2 presents a longitudinal section of the body (*C* in Fig. 1) of the calorimeter of one-half the real linear dimensions. The outer cylinder *a* is a tube of hard india-rubber (vulcanite),* 105

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* This material was selected on the ground of its remarkably low conducting power, a fact which has been strikingly brought out by the comparative measurements of J. Stefan (Wien. Acad. Ber. (2 Abth.); 74, 438–462). He finds, for example, that the true heat-conducting power of vulcanite is several times less than that of ordinary glass, whether considered for equal volumes or equal weights.

mm. long by 64 mm. in diameter inside, 1.5 mm. thick. The ends are round plates of the same material and thickness, and screw down over the extremities of the tube. The inner cylinder *b* is also a vulcanite tube of the same thickness, 22 mm. in interior diameter, passing snugly through a simple round hole in one end plate of the outer cylinder and screwing into a corresponding hole in the plate closing the other end.* The space between the inner and outer cylinders is uniformly but loosely filled with delicate turnings of vulcanite. Both ends of *b* are closed by very accurately fitted corks of the finest texture, free from all hard lumps, flaws, cracks or irregularities of surface. Through one of these corks *c* passes the stem of a mercurial thermometer *d*, specially made for this instrument, the scale bearing centigrade degrees of 6 mm. long, divided to tenths, and reading easily by estimation to twentieths of a degree, the scale running from 5° to 40° outside the cork.† The other cork *e* is solid. The length of the inner cylinder *b* is divided into two unequal parts by a diaphragm *f* of vulcanite of the same thickness with the tube itself, situated 47 mm. from the end bearing the thermometer and 59.5 mm. from the other end. This diaphragm is fixed in its place by three very small screws of vulcanite passing through the wall of the tube, and has in the centre a round hole *g* of 7 mm. in diameter. At three points equidistant from each other round this hole three bits of hard-drawn platinum wire *h*, each 37 mm. long and .35 mm. diameter, are firmly inserted on the side next the unperforated cork, their lower ends curved inward and their free ends sprung apart, so that the little platinum cylinder *i*, when dropped down between them, is grasped firmly enough to retain its place though the tube be inverted, and is supported exactly in the middle of the surrounding space, at equal distances from the inner surface of the tube, from the diaphragm, and from the cork *e*. The platinum cylinder *i*, intended to contain the substance whose specific heat is to be determined, is 28.5 mm. long by 12.5 mm. diameter, stiff

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* This inner cylinder might with advantage have been made somewhat smaller, best by shortening both cylinders a little and shifting the diaphragm somewhat toward the end containing the enclosed thermometer.

† As the temperature to which the substance to be examined is raised is determined directly from the boiling point of water under known barometric pressure, the absolute value of the scale of this thermometer, with which the temperature of the mercury in the calorimeter is determined, ought to be known. Comparison with a good standard instrument showed that such errors as exist are too small to sensibly influence the approximate results which alone can be obtained with the apparatus under notice.

enough, and slightly drawn in at the open end, so as to be securely closed by the cover *k*, while the two together weigh only a little over 6 grams. The supporting platinum wires weigh about .5 gram. A ring of cork *l*, 28 mm. wide and 5 mm. thick, encircles the outer cylinder *a* at the middle of its length, and is itself firmly grasped by a ring of hard wood *m*, 12.5 mm. wide and 5 mm. thick, in which, at two opposite points of the circumference, are the holes *n n* entered by the brass pins on which the whole turns. A weighed quantity of pure mercury—as I have used the instrument, about 220 grams—is placed in *b*, and can be shifted from one division of this cylinder to the other through the hole *g*, as by rotation on the bearings one end or the other is brought uppermost.

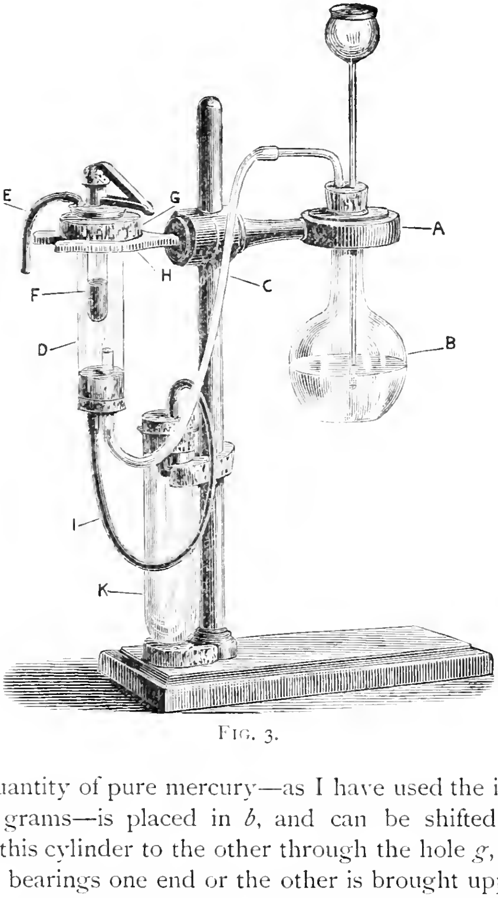

FIG. 3.

Fig. 3—to same scale as Fig. 1—illustrates the mode of heating, to the temperature of a current of steam, the specimen of material

whose specific heat is to be determined. *A* is a ring, sliding on and fixed at a convenient height on the upright rod of a filter stand, by which the flask *B* is supported over a lamp. *B* contains the supply of water for conversion into steam, the steam being carried by the india-rubber tube *C* into the lower end of the large glass tube *D*, from the upper end of which it escapes by the india-rubber tube *E*. The smaller glass tube *F*, closed at the bottom and placed concentrically within *D*, serves to contain the little platinum cylinder holding the specimen under examination. A large ring of cork *G* forms a handle, by which *D* may be taken up without burning the fingers, and during the heating this ring rests on the forked support *H*. The india-rubber tube *I* carries off water as condensed in *D* to the glass cylinder *K*. The tubes *C* and *I* are long enough to allow *D* to be lifted clear of its support and moved a foot or so without disturbing the rest of the apparatus, and without any interruption of the current of steam through *D*.

Fig. 4—to a scale of one-half the real linear dimensions—gives a vertical section of the heating-tube (*D* of Fig. 3) and its appendages. In this figure *a* is the outer glass tube, 145 mm. long and 45 mm. inner diameter, closed at top and bottom by corks *b* and *c*. Through the lower cork pass two bits of glass tube, each of 5 mm. bore, the one connected with the india-rubber tube *d* (*C* of Fig. 3) for the introduction of steam, the other leading to the tube *e* (*I* of Fig. 3), also of india-rubber, intended to drain away condensed water. The small bit of glass tube *f*, also of 5 mm. bore, passing through the upper cork, leads to the india-rubber tube *g*, about 140 mm. long, and serves for the escape of uncondensed steam at such a distance as to avoid any risk of either steam or drops of hot water getting into the calorimeter at the moment of transferring to it the platinum cylinder. The inner glass tube *h* is 15 mm. in diameter inside and 107 mm. long, closed at the lower end, and ground off squarely to a smooth edge at the top. It contains the little platinum cylinder *i* holding the specimen to be heated. After the introduction of this cylinder a loose plug of carded cotton fibre *k* is pushed into the mouth of *h*, which is then closed by a cover or lid formed of a piece of cork *l*, with a smooth lower surface, and carefully fitted so as to come down flat upon the mouth of the tube. *l* is attached to the long arm *m* of a little lever of wood, pivoted in a forked support at *n*, and capable of being very rapidly thrown

over backward by momentary pressure of the thumb on the short arm *o*, thus completely clearing the mouth of the tube *h*. *l* is weighted by a little piece of lead (a flattened buckshot) of 5 or 6 grams imbedded in the cork at its junction with *m*. *p* is a large cork ring, 18 mm. wide and 10 mm. thick, serving as a handle for *a* and as a shoulder by which it may rest on the forked support of the stand shown in Fig. 3. An outer jacket of stiff paper, containing cotton fibre or swan's down, may be placed round the glass cylinder *a* during the heating, but this, for the sake of clearness in the figure, is not shown.

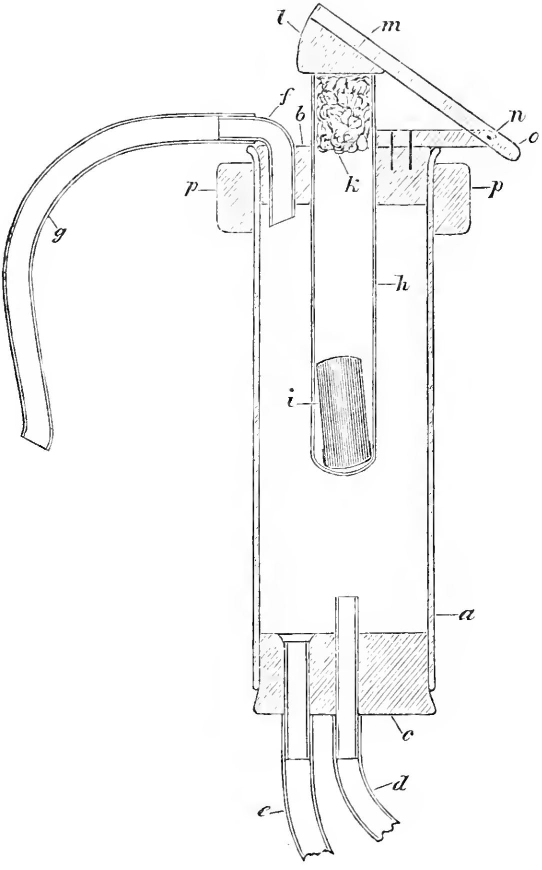

Fig. 4.

The preliminary observations are as follows:—It is first ascertained to what extent the temperature of the mercury in the calorimeter is raised by the metal running down from one end of the inner tube to the other during a given number of turns of the calorimeter on its bearings, the amount of motion in each direction being limited by the distance between the two corks (*H* and *I* of Fig. 1) which the thermometer stem touches at the top and bottom of its arc of movement. The rise of temperature is very small, as may be easily calculated from the extent of fall of the mercury, and is diminished by a part of the heat produced being absorbed by the vulcanite, the platinum and the material of the thermometer. Thus the actually observed rise of temperature was found to be but 0.06° C. for 100 *single* movements of the calorimeter, each transferring the mercury once from end to end of the tube. During this and all other experiments with the calorimeter it is kept in a large room of as steady temperature as possible and free from strong draughts of air.

The little platinum cylinder (*i* of Fig. 2) is now transferred to the bottom of the inner tube of the heating-apparatus (*h* of Fig. 4), in which it rests upside down, the loose plug of cotton wool *k* is inserted in the mouth of the tube *h*, over this the cork cover *l* is brought down, and, the connecting tubes being in position, a lamp is placed under the flask of water and the water boiled actively, but not so violently as to produce difference of pressure inside and outside the heating tube, thus sending a brisk current of steam steadily through the outer tube for half an hour or an hour, preliminary experiments with a small thermometer in the inner tube having shown that this is time enough to bring the contents of the tube closely up to the true temperature of the steam; the difference of temperature between the steam and the material to be heated was never found to be nearly as great as 1° or 2°, observed by Regnault in his experiments. The barometer and attached thermometer are now read, in order to admit of afterward calculating the true temperature of the steam. A few moments before the platinum cylinder is needed, the plug of cotton is quickly withdrawn, the cork cover dropped back to its place, and the current of steam somewhat increased by raising the lamp flame. The calorimeter, which has previously been kept in a part of the room far enough away from the heating-apparatus not to be sensibly affected by it, is now brought near to it, the thermometer is read and the reading recorded, the arm (*G* in Fig. 1) thrown back out of the way, the cylinder *C*, held lightly but firmly with the left hand, is brought nearly upright, with the thermometer downward, the upper cork (*e* of Fig. 2) loosened in its seat with the right hand so that it may be easily taken out, and then held ready for removal with the thumb and first finger of the left hand. The heating tube (*D* of Fig. 3) is lifted from its support by the cork ring *G*, which is placed as in a fork between the second and third fingers of the right hand, the palm of this hand being upward and the thumb lightly resting on the short arm (*o* in Fig. 4) of the little wooden lever which carries the cork cover *l*. The current of steam is not interrupted while the upper end of the tube (*h* of Fig. 4) is being brought close to the mouth of the calorimeter tube, and then, by quick simultaneous movements with both hands, the cork is momentarily withdrawn from the latter tube, the right thumb is pressed down so as to throw back the cover of the heating tube, and this tube is tilted so as to drop the platinum cylinder down into the calorimeter, where it is held in its central position by the elastic grasp of the three bits of platinum wire. The cork of the open end of the calorimeter is instantly replaced by the finger and thumb of the left hand, and the right hand used to insert it more firmly as soon as the heating tube has been quickly put back upon its support. The calorimeter is now carried back to its place in a distant part of the room, raising as it is carried the thermometer until it is between the two corks of the movable arm *G*, this arm being brought forward into position, and the body *C* of the instrument is gently turned* alternately up and down at such a rate as experience has taught will just allow the complete transfer of the mercury from one division of the tube to the other between the reversals, until the thermometer indicates that the maximum temperature due to the introduction of the heated platinum has been reached. A little practice soon teaches one to guess at about the time necessary for this, and the cylinder may then be stopped for a moment to allow of accurate reading, resuming the motion immediately afterward in order to see whether any further rise of temperature occurs. The loss of heat from the vulcanite is so slow that ample time is afforded for accurate observation of the thermometer. As an additional security, however, against the true maximum temperature being overlooked, it is convenient to have a little detached cylinder of mercury in the ther-

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* The projecting part of the solid cork *e* is used as a handle.

mometer tube as an index, like that of the common maximum registering thermometer, but reading from the head of the main column, and using the index merely to assure oneself that the reading is made before the temperature begins to fall. The number of swings made by the calorimeter has been counted as it was turned. A comparison of the initial temperature of the mercury with that finally reached after the introduction of the platinum cylinder, gives the heating effect of the latter plus that due to the agitation of the mercury, as previously determined, for the number of swings made. Subtracting the latter, and after several repetitions of the experiment taking the mean of the results, reduced to the same interval of temperature passed through by the platinum,* the practical effect of the latter in heating the mercury, while itself cooling a given number of degrees, is known.

If now the specific heats of two solid bodies are to be compared, a specimen of each in succession is accurately weighed off, enclosed in the platinum cylinder, raised to the temperature of the steam in the heating apparatus, transferred to the calorimeter, and the effect upon the temperature of the mercury observed, precisely as in the experiment above described with the empty platinum cylinder. Aside from the time occupied in heating up the specimen to be examined, an experiment takes but two or three minutes. It is desirable to take such a quantity of the substance as shall occupy the greater part of the capacity of the cylinder, since otherwise, if the platinum cover be not tightly fitted on, a little mercury may be forced into the cylinder in consequence of the contraction of the enclosed air as it cools down. Good results have been obtained, however, with quantities ranging from .8 gram up to 25 grams. From the heating effect produced in the calorimeter in each experiment is to be deducted that due to the platinum cylinder for the interval of temperature passed through, and to the agitation of the mercury for the number of turns made of the body of the instrument. If the second experiment follow immediately after the first there will generally be little difference between the initial temperatures and final temperatures respectively of the bodies examined, but of course the results are always to be reduced by calculation to the same interval passed through.

To restore the temperature of the calorimeter quickly after an ex-

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* The specific heat of platinum, as of mercury, may of course be considered as uniform within the range of variation of the temperatures employed.

periment to that of the room or very near this, a separate cork is provided, to take the place of *e* in Fig. 2, through which passes a sealed test-tube containing mercury. This mercury is cooled a good deal below atmospheric temperature by immersion of the test-tube for a little while in a larger quantity of mercury contained in a beaker and either placed out of doors in cold weather or surrounded by ice water. On inserting the cork in its place at the end of the inner cylinder of the calorimeter, and turning the body of the instrument up and down a few times, the tube of cold mercury reduces the temperature of that which surrounds it until the thermometer reads a little below the temperature of the room. Removing the cold mercury tube and cork, replacing the latter by the solid cork *e*, turning this end of the calorimeter downwards, taking out the thermometer from the other end, to cool it in like manner by immersion of the bulb in cold mercury, and to set the index, and then replacing it, turning the thermometer end down again, taking out the cork *e*, and allowing the instrument to stand for a little while with the inner cylinder open, the temperature of the room is fully recovered.

In no case is the whole heating effect of the platinum cylinder and its contents expended upon the mercury, a portion of the heat going to raise the temperature of the vulcanite, the end corks, the little platinum wires, and the enclosed portion of the thermometer. But the character and quantity of all these substances sharing in the reception of heat being constant, and the circumstances under which heat is given off and received being rendered practically uniform, a large and nearly a constant fraction of the whole heating effect is expended on the mercury, so as to render the results as obtained practically useful measures of the heat given out by the cylinder and its contents. The rate at which heat is taken up from or given off to surrounding matter by the well protected mercury in the calorimeter is so slow, the greatest difference of temperature which need exist between the interior and exterior is so small, and the time necessary for an experiment is so short—but two or three minutes,—that the correction employed by Favre for the rate at which the mercury in his calorimeter was heating or cooling from without during an experiment (obtained from observations before and after) need not be, although of course it might be, applied.

The quantity of the substance taken for examination may conveniently be such as to produce a rise of temperature of the mercury to the extent of 5 or 6, or at most 8 degrees, and if the specific heat of the substance can be guessed at, or be roughly determined in a first experiment, greater accuracy may be attained by taking such weights of the substance itself and of that with which it is to be compared as shall produce very nearly the same heating effect. If the initial and final temperatures shown by the thermometer be made the same or nearly the same in successive experiments, the correction for the portion of the stem outside the calorimeter becomes constant, and so may be neglected in this merely comparative method. Further, instead of comparing the effect in every case with that of a single standard body, I prefer to take for comparison any substance of which the specific heat is already well determined, and whose general character, as regards specific gravity, conducting power, etc., resembles that of the substance of which the specific heat is to be examined, thus using for the purpose of comparison with substances of analogous character such bodies as platinum, mercury, calcareous spar, sodium chloride, water, benzene, etc. The substances compared should be, as far as possible, in the same state of compactness or subdivision. When a liquid is to be examined the specimen is enclosed in a tube of very thin glass, as nearly as possible filling the platinum cylinder, and with a drop of mercury used to close up the greater part of the space round the side and bottom, the heating effect of the kind and weight of glass used being determined beforehand, and the platinum cylinder with its contents weighed on withdrawal from the calorimeter so as to prove that the little drop of mercury inside has not been increased by any of that in the calorimeter or diminished by any escaping into the latter. Care is to be taken that in all respects, prevailing atmospheric temperature, quickness of manipulation, etc., the conditions of comparison be made as nearly as possible the same. This is rendered easy by the short time required for the experiments.

The two main features peculiar to the little calorimeter now described are simply the employment of mercury instead of water as the liquid to be heated, and the comparison, not of the total amounts of heat given out by different bodies in cooling, but of fractions of the same rendered as nearly as possible equal.

The employment of mercury as the material whose temperature is to be raised by the heat given out by the substance experimented on has certain advantages: 1st. For equal bulks mercury experiences 2.2 times the increase of temperature that water does for the same amount of heat received. The volume of mercury used may therefore be made quite small while retaining command of sufficiently accurate reading of the change of temperature produced. 2d. The superior conductivity of mercury and its low specific heat facilitate the transfer of heat from the cooling body, shortening the time of the experiment, and thus diminishing the loss of heat through the solid material of the calorimeter, whose properties in the respects mentioned are, as they should be, the reverse of those of the mercury. 3d. Mercury does not sensibly vaporize at such temperatures as are required for the purpose in question, and hence no loss of heat on this account is to be feared. In experiments like those of Regnault, if made with a small quantity of water in an open vessel, the error due to evaporation, and consequent loss of latent heat, may become considerable, or may require for correction troublesome repetition of weighings of the water used. 4th. For the same reason the original quantity of mercury taken remains unchanged, and hence the instrument is always ready for use. To secure this convenient condition, the inner cylinder of the calorimeter is only to be opened with caution, over a little tray of glazed card-board, and any globules, even the most minute, of mercury which may be found adherent to the corks, thermometer bulb, or cold mercury tube, are to be swept together, as is easily done with a small camel's-hair pencil, and returned to the cylinder.

This application of mercury is to be distinguished from that involved in the calorimeter of Favre and Silbermann, and in that recently described by Prof. Stewart* and Messrs. Gee and Stroud,† in both of which the expansion of mercury in the calorimeter itself is directly measured, and used to determine the rise of temperature.

As regards the second peculiarity of the instrument now described, it is obvious that, in any arrangement for measuring the heat given out from one body in cooling by applying it to raise the temperature of another, it is impossible to prevent loss by conduction and radiation, and by making the vessel of material of high conducting power and counting it in with its contents, the difficulty is but shifted from the inside to the outside of its walls. On the other hand, it is clearly not necessary that the whole amount of heat given out by the cooling body be obtained in measurable form; it would come to quite the same thing (as far as the determination of specific heats is concerned) if we could secure the measurement in all cases of a constant fraction of it. It is not pretended that

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* Proc. Manchester Lit. and Philos. Soc., March 4, 1879.

† L., E. and D. Philos. Mag., Sept. 1880, p. 171.

this latter result has been fully secured in the apparatus now described, nor is its use proposed as a general substitute for more exact methods, but that it is capable of giving a very fair approximation to such result is, I think, shown by the following examples of determinations of specific heat which have been thus obtained. The figures are not carried in calculation beyond three places of decimals:

A.	B.	C.	D.	E.
Substance examined.	Substance used for comparison.	Spec. heat assumed for substance in col. B.*	Spec. heat found for substance in col. A.	Spec. heat previously recorded for substance in col. A.*
Silver,	Platinum,	.0323 †	.055 .058 .057	.057 (Regnault) .056 (Kopp) .0559 (Bunsen)
Copper,	"	"	.090 .098	.0951 (Regnault) .093 (Kopp) .0924 (Wullner)
Iron,	"	"	.110 .106 .110	.1138 (Regnault. .112 (Bunsen)
Mercury,	"	"	.032 .034 .033 .032 .031	.0333 (Regnault) .0337 (Winkelmann) .0334 (Petersson and Hedelius)
Ferric oxide, (specular iron)	Calcium carbonate, (Iceland spar)	2073 ‡	.159 .165 .163	.1669 (Regnault) .166 (Neumann) .154 (Kopp)
Barium sulphate, (heavy spar)	"	"	.109 .104	.1128 (Regnault) .108 (Kopp) .1088 (Neumann)
Potassium nitrate, (cryst.)	Sodium chloride, (cryst.)	.2150 §	.226 .238	.23875 (Regnault) .232 (Kopp) .2343 (Neumann)
Cane sugar, (cryst.)	"	"	.298 .292	.301 (Kopp)
Ethyl alcohol,	Water,	1.0044 ‖	.628 .640 .637	.6769 (calc. from Regnault) .6138 (Schüller) .6273 (Dupré and Page, cor. by Schüller's formula) .66885 (calc. from Winkelmann)
Sulphuric acid	"	"	.368 .355	.343 (Kopp) .3542 (Pfaundler)

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* Where the authorities referred to for the numbers in these columns give the means of ascertaining the spec. heat for the particular range of temperature involved in my experiments, this number is quoted.

† .0323 (Violle) .0324 (Regnault).

‡ .2086 (Regnault) .206 (Kopp).

§ .2140 (Regnault) .216 (Kopp).

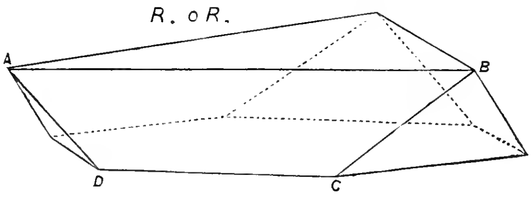
‖ 1.0039 (Henrichsen) 1.005 (Regnault).

ON JAROSITE FROM A NEW LOCALITY.

By George A. König.

The material is composed of single crystals and crystal aggregations, which rest (for the most part) on a black, brilliant layer of thurgite (hydrohematite). After having ascertained preliminarily the identity of this material with jarosite, I was led to a thorough examination in the hope of establishing the real composition of this compound.

Crystallographical characters.—On some specimens the crystals show a very marked cubical habitus, but one visible corner appearing slightly truncated, inducing me at first to the determination of the mineral as pharmacosiderite. But if this was correct, then the truncation must be a tetrahedron, which I believe had never been noticed on that species. However, when I visited the mine, I found the habitus on most specimens decidedly rhombohedral, with tabular development parallel to the basis, as the accompanying figure shows. Examined with a lens the crystals are very beautiful, and exhibit a remarkable adamantine lustre. But their softness and the strong cleavage present considerable difficulty to any attempt at procuring a crystal fit for measuring. After many failures I succeeded in the separation of a crystal about two millimeters long by one mm. in breadth. (See figure.) From this I obtained the normal angles for the marginal edge AD=89° 15′ (89° 13′ to 89° 17′).



Basal edge AB=55° 15′ with an uncertainty of ± 4

The pole edge is therefore 89° 15′ and c=1.250. The calculated basal edge is 124° 44′, which agrees very well with the observed mean of 124° 45′.

In Dana's System of Min., 5 edit., the angles are given:

Pole edge=88° 58′; Basal edge=124° 32′; c=1.2584.

This deviation is not inconsiderable, but I have reason to assume that my material is superior to that upon which the latter result was obtained, since Dana says, as a character of the lustre, "dull to a little shining." The lustre of my objective crystals is *adamantine* on the faces and resinous on the fracture, resembling sphalerite very much in this respect. The color is deep reddish brown, rarely yellow in crystals, but generally so for the crusted aggregations; quite transparent; powder light yellow.

Specific gravity=3.144, made upon material under *c*, and consequently not quite correct, but nearly so, since the reduction caused by 2.6 per cent. of quartz is compensated by the increase of 8.67 per cent. of thurgite. The blowpipe reactions are indicated by the composition.

Analyses.—I should have preferred for analysis the fine single crystals, but an attempt furnished such meagre quantitative result that recourse had to be had to the material aggregated into crusts. These were obtained from several specimens, and whilst some appeared very pure, the greater part showed under the lens an admixture of chalcedony and grains of black thurgite. But the jarosite itself was throughout in crystals, not the least massive, and the question whether such material could be relied upon for the solution of a theoretical question had to be answered in the affirmative. For to this end only the ratio between alkali, sulphur and water was necessary. Analyses *a* and *b* are made upon the same sample, which contained only traces of SiO_2; *c*, *d* and *e* were made upon a second sample, which held 2.60 per cent. SiO_2 as quartz.

a. 0.2000 gr. was kept at a bright red heat until the weight remained constant. It gave 0.0664 loss by ignition=32.20 per cent. H_2O+SO_3.

b. 0.2500 gr. dissolved in HCl gave 0.1270 Fe_2O_3.

$$\begin{cases} 0.0435\ (K_2Na_2)SO_4;\ 0.1005\ K_2PtCl_6=0.0356\ K_2SO_4. \\ -0.0356=0.0079\ Na_2SO_4. \end{cases}$$

(Determination of sulphur was lost.)

c. 0.5000 gr. gave 0.4190 $BaSO_4$.

$$\begin{cases} 0.0640\ (KNa)Cl;\ 0.1840\ K_2PtCl_6=0.0561\ KCl. \\ -0.0561\ KCl=0.0079\ NaCl. \end{cases}$$

0.2550 Fe_2O_3.

0.0130 SiO_2.

d. 0.5000 gr. gave 0.4160 $BaSO_4$.

e. 0.2527 gr. kept at bright red heat until constant weight was reached, 0.0809 loss by ignition = 32.01 per cent. H_2O+SO_3.

In the following table these figures are reduced to 100 after deducting the quartz:

		a.	*b.*	*c.*	*d.*	*e.*
Fe_2O_3	=	...	50.80	52.36	...	...
K_2O	=	...	7.76	7.30	...	...
Na_2O	=	...	1.36	0.90	...	...
SO_3	=	... }	..	29.34	29.32	... }
H_2O	=	32.20 }	...	...	...	32.54 }

Analysis *c* agrees with *b* fairly, being made upon another sample, but it deserves greater credit for accuracy, as it was made upon double the quantity of substance. The two analyses also contain the unknown variable thurgite, and are therefore not comparable. The values obtained under *c*, *d*, *e*, shall be made exclusively the basis in the following calculation. In order to obtain the percentage of water we find the SO_3 in combination with K_2O and Na_2O first, as this was not volatilized by heating.

Then, $32.54-29.33+6.18+1.16=10.55$ H_2O ; and now,

$Fe_2O_3 =$	52.36	$Fe_2 = 36.65 : 112 = 0.3272$	
$K_2O =$	7.30	$K_2 = 6.06 : 78.4 = 0.0773$	} 0.0919
$Na_2O =$	0.90	$Na_2 = 0.67 : 46 = 0.0146$	}
$SO_3 =$	29.33	$S = 11.73 : 32 = 0.3665$	
$H_2O =$	10.55	$O = 34.78 : 16 = 2.1737$	
	100.44	$H_2O = 10.55 : 18 = 0.5861$	

$$(KNa)_2 : cS : Fe_2 : O : H_2O =$$

$$0.0919 : 0.3665 : 0.3272 : 2.1737 : 0.5861 =$$

$$1 : 3.988 : 3.5604 : 23.64 : 6.377$$

Now the ratio $K_2 : S$ is absolutely as $1 : 4$; some Fe_2O_3 and water being present as thurgite, the empirical formula follows:

$$K_2Fe_6S_4O_{22}+6H_2O.$$

In thurgite there are 4 iron atoms combined with 1 water, hence 0.5604 double atoms with 0.2802 molecule of water, leaving an excess of water of 0.1 molecule. For the analyzed substance we obtain in 100:

(Jarosite)	$K_2Fe_6S_4O_{22}+6H_2O$	= 91.57
(Thurgite)	$Fe_4H_2O_7$	= 8.84
(Excess)	H_2O	= 0.03
		100.44

Thus it is demonstrated, beyond doubt, that jarosite is in form and structure identical with alunite, that in fact both form only *one* species, in which Al_2 and Fe_2 may enter singly or in any proportion, replacing each other.

Rammelsberg[*] separates jarosite and gelbeisenerz, assuming that the former may have the formula of alunite, adducing Th. Richter's analysis,[†] which comes near it, if the loss of 1.1 per cent. be added to K_2O. Ferber's analysis[‡] is either incorrect or made upon a mixture of jarosite with some other sulphate, and belongs to the indefinite group of "yellow ochre."

Dana combines jarosite with gelbeisenerz into one species, excluding Richter's analysis as "incomplete," for what reason I cannot see, since Rammelsberg gives it as "complete"; but he too remarks that jarosite may have the formula of alunite. It will be well, hereafter, to follow Rammelsberg's precedent and retain the name *gelbeisenerz* for indefinite compounds, in which jarosite probably forms the larger portion; or such analyses as Scherer's, who gives all alkali as Na_2O, for, if this be correct, it makes a new species, from the same reasons which separate jarosite from alunite, *i. e.*, the replacement of one metal for another within the same molecule; but the analysis is probably incorrect. Prof. Benjamin Silliman, Jr.,[§] communicated his discovery of jarosite at the Vulture mine, Arizona, without analysis. After the appearance of my analysis of jarosite in the October signature of the Proceedings Academy Natural Sciences of Philadelphia, Professor Silliman kindly sent me a specimen from that locality, which resembles the Colorado mineral very much, but the crystals are much less brilliant and perfect. The professor also states that his analysis, which will be published shortly, confirms my result.

The material for this investigation was collected by myself during the past July. It occurs in a prospect for "carbonates" in porphyry, six miles east of south Arkansas, and two miles north of the river at an elevation of about 600 feet above the latter, in Chaffee County, Colorado. The claim is called the "Iron Arrow." The prospect was made upon the marked iron stain of the rock, the float showing much red ironstone, which is so characteristic of the Leadville formation. Examination convinced me that there is no contact formation here, but many local lenticular masses of thurgite, sometimes of high grade and nearly destitute of phosphorus, but degenerating mostly into a ferruginous hornstone.

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[*] Mineralchemie, 2 Aufl. 1875, p. 2793, f. [†] B. H. Zg. 1852. [‡] Ibid. 1864. [§] Am. J. Sc. 1879.

Nearly every piece on the dump showed jarosite. But at no other outcrop showing similar conditions, and there are many, could I find the mineral in central or southwestern Colorado.

University of Pennsylvania, *Nov.*, 1880.

ON BEEGERITE, A NEW MINERAL.

By George A. König.

The small specimen on which the present investigation was made is seen to be made up of an aggregation of three mineral substances. Probably one half is quartz, in well defined small crystals and grains; the other half consists of a massive light gray mineral, and again of crystals showing a darker gray color, but exhibiting a very strong metallic lustre. Examination proved the chemical identity of the two latter substances, the difference of color resulting probably from the strong reflection of the light from the crystal faces.

Crystallographic symmetry.—The habit of the crystals is orthorhombic after the combination $P\infty \, . \, \infty\breve{P}\infty \, . \, \infty\breve{P} \, . \, \infty\bar{P}$. The crystals are small, so that their faces can only be seen distinctly by means of a good lens, and so grown into groups that single and measurable individuals are very rare. A first trial gave for the zone $P\infty$ the following readings:

0°0′, 43°10′, 70°20′, 113°30′, 125°25′, 180°0′, 250°0′, 305°33′, 348°45′, 360°, but since a close examination shows only 6 faces in the zone, it is clear that images were recorded from other crystals of the group. Nevertheless one can readily combine the following normal angles: 70°20′, 55°5′, 54°33′, 70°35′, 54°27′, and these agree nearly with the normal angles of the isometric combination $O \, . \, \infty O \infty$. From the same crystal also were obtained normal of edge BD=54°55′; B, D=54°50′. Another crystal was now selected (represented by the figure), and could be so well isolated that the

O. ∞O ∞.

edges AE, BF, BD, BC and the angle ACA′ were measurable without secondary reflections, giving the following mean of 3 readings:

B′F′= 55°0′; AE=70°13′; BF=54°47′; BD=54°28′; BC= 54° 20′; angle ACA′=90°0′; only the images giving the last angle (ACA) were perfect. However, when the theoretical angles of 70°32′ and 54°44′ were fixed on the goniometer, the strongest light of the undefined images was observed near the cross-hair. The angle of 90°0′ having been measured sharply, there seems to be no reason to doubt the *isometric symmetry* of the mineral, the combination $O \infty O\infty$ equal being the one most common on galenite. Cleavage is cubical, as strongly as galenite.

Specific gravity was determined on 0.6627 gr. of the mixed minerals in a small pyknometer weighing, when filled with water, 3.5095 gr. Loss of weight=0.1322; quartz=0.1703; pure mineral 0.4924. Spec. gravity of quartz being 2.65, the specific gravity of the new mineral is $\frac{0.4924}{0.0677}=7.273$.

Before the blowpipe the mineral acts like a mixture of galenite and bismuthinite, with a small quantity of copper. It decripitates, and is dissolved by concentrated hydrochloric acid, slowly in the cold, but rapidly in the heated acid. The reactions were made on the pure crystals and on the massive mineral, and found to be identical for both.

Analysis.—By reason of the limited quantity of material, a mechanical elimination of the quartz was not attempted, as quite unnecessary in fact, as it could be accurately estimated in each analysis and subtracted. But in the material of analyses *a* and *b* the massive mineral was excluded as much as possible, while the powder on which *c*, *d* were made contained crystals and massive mineral in about equal proportion.

a. 0.5000 gr. decomposed with hydrochloric acid gave
0.0890 quartz.
0.3832 $PbSO_4$=0.2618 Pb.

b. 0.5000 gr. decomposed with conc. nitric acid and potassium chlorate, gave
0.4900 quartz+$PbSO_4$ (extracted with $Na_2S_2O_3$).
0.0930 quartz, and by difference,
0.3970 $PbSO_4$=0.2711 Pb.

c. 1.0000 gr. decomposed with HCl and H_2S condensed in an ammoniacal solution of cadmium, gave
0.3106 quartz.

0.4855 CdS = 0.1083 S.
0.1775 basic chloride of bismuth = 0.1420 Bi.
0.6485 $PbSO_4$ = 0.4437 Pb.

d. 0.6400 gr. decomposed with conc. nitric acid alone, gave
0.4720 quartz + $PbSO_4$. The lead sulphate was dissolved by continued treatment with hot nitric acid, and left 0.1955 quartz; hence,
0.2765 $PbSO_4$. The first filtrate being very acid in order to remove all bismuth, a considerable quantity of $PbSO_4$ had entered into it; $Ba(NO_3)_2$ being added, and evaporated to near dryness, the $BaSO_4$ was converted into carbonate by fusion with Na_2CO_3, and from acidulated filtrate the sulphuric acid again precipitated.
0.1486 $PbSO_4$.

0.4251 total $PbSO_4$	in 0 2765 $PbSO_4$	S =	0.0287
0.2585 $BaSO_4$	...	S =	0.0355
0.0120 CuO	= 0.008 Cu	S =	0.0642

(The determination of bismuth in this analysis was lost.)

In the following table these results are calculated in per cent. after deducting the quartz:

		a.	*b.*	*c.*	*d.*	mean.		quotients.
Pb	=	63.66	64.60	64.59	64.07	64.23 : 207.2	=	0.309
Bi	=	...	...	20.59	...	20.59 : 208	=	0.0990
S	=	...	...	15.71	14.23	14.97 : 32	=	0.468
Cu	=	...	...	...	1.70	1.70 : 126.4	=	0.013
						101.49		

or very nearly the ratio Bi : Pb : S = 2 : 6 : 9.3.

Pb_6	=	207.2 × 6	=	1243.2	63.84
Bi_2	=	208 × 2	=	416.0	21.36
S_9	=	32 × 9	=	288.0	14.78
				1947.2	99.98

Considering the difficulties connected with the separation of lead and bismuth, the agreement of the results obtained with the calculated percentages must be considered quite satisfactory. The empirical formula of the mineral is therefore

$$Pb_6Bi_2S_9 = 6PbS + Bi_2S_3.$$

This may be regarded as an interesting example of the mass influence on the crystallization of compound molecules.

Whilst the isometric molecule PbS preponderating 6 times, determines entirely the symmetry, the orthorhombic molecule Bi_2S_3 affected merely a prismatic habitus. From the composition it is easily understood that the other properties of this compound coincide nearly with those of galenite. Qualitatively related with the new mineral are the two species cosalite* and schirmerite† described by Dr. F. A. Genth. But the complete absence of silver in the new mineral is very notable.

Schirmerite = $(Ag_2Pb)_3Bi_4S_9$.
Cosalite = $(PbAg_2)_2Bi_2S_5$.
Beegerite = $(PbCu)_6Bi_2S_9$.

Schirmerite has only been found massive, and cosalite in striated prisms of undefined symmetry. But it may be inferred by analogy that both are orthorhombic, because of the preponderance of the orthorhombic Bi_2S_3. Of same molecular structure as beegerite is stephanite, $Ag_{12}Sb_2S_9$, which is so typically orthorhombic, because Ag_2S is here as acanthite orthorhombic, with the orthorhombic stibnite.

The new mineral occurred on the Baltic Lode of the Geneva Mining Company, near Grant Postoffice, Park County, Colorado. I received the only specimen supposed to be in existence from Mr. Hermann Beeger, of Denver, Colorado, and I named the species in honor of this gentleman as a recognition of his services to metallurgy in Colorado.

It may be remarked that the schirmerite occurred on the Treasury lode of the same district.

UNIVERSITY OF PENNSYLVANIA, *Nov.*, 1880.

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*Am. J. Sc. 2, 45, 319.

† Proceedings Am. Philos. Society, 1874.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

VIII.—RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

THE SYNTHESIS OF ANTHRACENE AND PHENANTHRENE FROM ORTHOBROMBENZYLBROMIDE.[*]

By C. Loring Jackson and J. Fleming White.

Discovery of Anthracene.

The first notice of anthracene (under the name paranaphtaline) appears in a paper[†] on compounds of hydrogen and carbon, published by Dumas and Laurent in 1832. They obtained it in the fractional distillation of coal-tar from the portions with the highest boiling-point, but did not succeed in purifying it, as is shown by the melting-point 180°, and the formula $C_{15}H_6$. Laurent,[‡] in 1835, studied its oxidation product "paranaphtalese" (anthraquinone), and in 1837[§] proposed the name anthracene for it; but neither of these papers, nor one[||] also published by Laurent in 1839, gives a satisfactory account of the hydrocarbon, as the quantity at his disposal was too small for complete purification.

The first accurate characterization of anthracene is due to Fritzsche,[¶] who, in 1857, obtained from coal-tar a hydrocarbon with the formula $C_{14}H_{10}$, and melting-point 210°, forming a picric acid compound melting at 170°, but he did not identify it with the anthracene of Laurent. This was reserved for Anderson,[**] who, in 1861, repeated Laurent's experiments on a larger scale, and showed that his anthracene had the formula $C_{14}H_{10}$, melted at 213°, and was the same as Fritzsche's unnamed hydrocarbon.

In 1867, Fritzsche[††] described the preparation of his reagent (dinitroanthraquinone), and its use in the detection and purification of hydrocarbons; and Berthelot[‡‡] reviewed all the previous work upon anthracene, determining its boiling-point 360° for the first time.

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[*] Presented to the American Academy. Communicated by the Authors.

[†] Ann. Chim. Phys. 50, 187. [‡] Ibid. 60, 220. [§] Ibid. 66, 149. [||] Ibid. 72, 415.

[¶] St. Petersburg Acad. Ber. 1857. Jour. pr. Ch. 73, 286. [**] Ann. Chem. Pharm. 122, 294.

[††] Zeit. für Chemie, 1867, 289. [‡‡] Bull. Chem. Soc. 8, 231.

The next important paper on the subject appeared in 1869, when Fritzsche,* on account of its behavior with his reagent, pronounced anthracene a mixture of two very similar hydrocarbons, which he called photene, melting-point 210°–212°, and phosene, melting-point 193°.

In the following year (1870) general attention was attracted to anthracene by the appearance of Graebe and Liebermann's famous paper† on anthracene and alizarine, in which they not only proved that alizarine was dioxyanthraquinone by preparing it synthetically from anthracene, but described a large number of derivatives of anthracene, giving for the first time the melting-point of anthraquinone 273°. They showed, too, that Fritzsche's photene was identical with anthracene, but were unable to obtain his phosene, which Barbier‡ four years later showed was probably a mixture of anthracene and phenanthrene.

Syntheses of Anthracene.

In describing the syntheses of anthracene, all those made by the same method will be grouped together, and these groups will be taken up in the order of their discovery.

1. Limpricht§ was the first (in 1866) who made anthracene synthetically, unless, indeed, one of the products obtained by Märcker,‖ in 1865, from the action of heat on tolallylsulphide must be considered anthracenesulphide, but there seems to be no sufficient ground for this supposition. Limpricht's method consisted in heating benzylchloride with water in a sealed tube to 190° for eight hours; the products were benzylether, an oil $C_{14}H_{14}$, and anthracene.

Van Dorp,¶ in 1872, obtained the same result, and proved that the oil $C_{14}H_{14}$, which Limpricht had thought was dibenzyl, is benzyltoluol. Finally Zincke,** in 1874, showed that this reaction resembled that of zinc-dust on a mixture of benzylchloride and benzol, and succeeded in isolating a chloride $C_6H_5CH_2C_6H_4CH_2Cl$ and a complex hydrocarbon. He proved, further, that this synthesis was of little value in determining the constitution of anthracene, since neither anthracene nor benzyltoluol was present in the product of the reaction, but they were formed during distillation by the breaking up of the more complex substances just mentioned.

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* Zeit. fur Chemie, 1869, 387.

† Ann. Chem. Pharm. Supp. 7, 257. A preliminary notice appeared in 1868, Ber. d. ch. G. 49.

‡ Comptes rendus, 79, 121.

§ Ann. Chem. Pharm. 139, 308.

‖ Ibid. 136, 94.

¶ Ber. d. ch. G. 1872, 1070. Ann. Chem. Pharm. 169, 207.

** Ber. d. ch. G. 1874, 276.

2. In the year after Limpricht's synthesis was published, Berthelot, in developing his general method for the synthesis of complex hydrocarbons by passing simpler ones through a porcelain tube, heated to redness, obtained anthracene[*] from toluol (confirmed by Graebe[†] in 1874), xylol, cumol, and mixtures of benzol with ethylene,[‡] and of benzol with styrol; also traces of it by heating acetylene to redness in a glass tube over mercury. The same method was applied successfully by Van Dorp[§] to benzyltoluol, that obtained from benzylchloride toluol and zinc-dust, as well as that from benzylchloride and water; by Kramers[‖] to phenol (yellow heat); by Claus and Suckert[¶] to azobenzol; and by Barbier[**] to the mixture of toluol with benzol, and to that of diphenyl with ethylene, although the latter yielded only traces of anthracene. Barbier, in 1874, substituted for red-hot porcelain tubes vacuous sealed glass tubes heated to dull redness for a few minutes, and obtained in this way anthracene from benzyltoluol, phenylxylol, diphenylmethane, and liquid ditolyl. While Behr and Van Dorp[††] obtained the same result a year earlier by passing liquid benzyltoluol, or liquid tolylphenylketone over gently heated plumbic oxide. The synthesis from orthotolylphenylketone by the aid of heat has been recently repeated by Ador and Rilliet.[‡‡]

3. The next synthesis of anthracene was published in 1872 by Kekulé and Franchimont,[§§] who obtained a small quantity of anthraquinone from the by-products of the distillation of calcic benzoate. Their results were confirmed by Behr[‖‖] and Staedel.[¶¶]

4. Related to this method is that of Barth and Senhofer,[***] published in 1873, which consists in heating oxybenzoic acid alone, or with sulphuric acid.

5. In 1873, also, anthracene was first obtained by Zincke's reaction; for, although Zincke[†††] had not succeeded in finding it, Radziszewski and Zaleski[‡‡‡] got it from zinc-dust, benzylchloride and benzol, and Paterno and Filetti[§§§] by the action of zinc-dust on a mixture of benzylchloride and phenol; the latter, however, think that it is not formed directly, but by a secondary reaction from the benzylphenol, and this view is supported by a paper published in

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[*] Bull. Chem. Soc. 7, 222.

[†] Ber. d. ch. G. 1874, 48.

[‡] Bull. Chem. Soc. 7, 279.

[§] Ber. d. ch. G. 1872, 1070. Ann. Chem. Pharm. 169, 207.

[‖] Ann. Chem. Pharm. 189, 131.

[¶] Ber. d. ch. G. 1875, 37.

[**] Comptes rendus, 79, 121, 660, 810. Also, Ann. Ch. Phys. ser. 5, 7, 515.

[††] Ber. d. ch. G. 1873, 753.

[‡‡] Ibid. 1879, 2298.

[§§] Ibid. 1872, 909.

[‖‖] Ibid. 1872, 971.

[¶¶] Ibid. 1873, 178.

[***] Ann. Chem. Pharm. 170, 100.

[†††] Ber. d. ch. G. 1873, 137.

[‡‡‡] Ibid. 1873, 810.

[§§§] Gazz. Chim. 1873, 121.

the following year by Zincke and Weber,[*] who obtained it from a mixture of zinc-dust, benzylchloride and toluol, but suppose that all the anthracene is formed by the breaking up of complex hydrocarbons during the subsequent distillation, in the same way that it is formed from the product of the action of water on benzylchloride. More interesting, therefore, is the synthesis of Piccard,[†] who obtained anthraquinone by the action of zinc-dust on the chloride of phthalic acid and benzol at 220°.

Under this head should come also the recent experiments of Friedel and Crafts,[‡] who, among their beautiful syntheses with aluminic chloride, made anthraquinone from the same mixture, and finally of Ador and Rilliet,[§] who, in 1879, obtained it from the chloride of orthotoluic acid, benzol and aluminic chloride.

6. Paterno and Filetti,[‖] in a paper published somewhat later, in 1873, describe the synthesis of anthracene by the distillation of benzylphenol with phosphoric pentoxide.

7. In the same year appeared a paper by Grimm,[¶] from Baeyer's laboratory, describing the synthesis of chinizarine from phthalic anhydride, hydroquinone and sulphuric acid; while in 1874, Baeyer and Caro[**] found that phthalic anhydride yielded, with phenol, benzolsulphoacid, anisol, anisic acid, or salicylic acid, either oxyanthraquinone or erythroxyanthraquinone, both of which give alizarine by fusion with potassic hydrate; with pyrocatechin, guaiacol, or protocatechuic acid, alizarine; with hydroquinone (see Grimm), quinic acid, thiochronic acid, or the α and β sulphoacids of hydroquinone, chinizarine. Still later, in 1875,[††] they added chlorphenol, boiling-point 218°, to the list of substances which form chinizarine, and converted chinizarine into purpurine by oxidation.

In his last paper[‡‡] on phtaleines and their derivatives, published in 1880, Baeyer shows their close relation to the anthracene group, ordinary phthalidine being dioxyphenylanthranol, while a corresponding compound can be obtained from triphenylmethanecarbonic acid.

8. The syntheses of anthraquinone from benzoylbenzoic acid also begin in 1873, when Plascuda and Zincke[§§] obtained a little in oxidizing crude benzoyltoluol. In the following year Behr and Van Dorp[‖‖] made it by oxidizing tolylphenylketone, and somewhat

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[*] Ber. d. ch. G. 1874, 1153.

[†] Ber. d. ch. G. 1874, 1785.

[‡] Comptes rendus, 84, 1450.

[§] Ber. d. ch. G. 1879, 2298.

[‖] Gazz. Chim. 1873, 251.

[¶] Ber. d. ch. G. 1873, 506.

[**] Ibid. 1874, 968.

[††] Ber. d. ch. G. 1875, 152.

[‡‡] Ann. Chem. Pharm. 202, 36.

[§§] Ber. d. ch. G. 1873, 906.

[‖‖] Ibid. 1874, 16.

later in the same year converted β-benzoylbenzoic acid into anthraquinone* by heating it with phosphoric pentoxide, a process which ran smoothly and yielded 26 per cent. of the theoretical amount, whereas the para-acid, under the same conditions, gave no anthraquinone whatever. The formation of traces of anthraquinone from the distillation of calcic benzoate alone, and of benzoic acid with phosphoric pentoxide, they ascribe to the previous formation of β-benzoylbenzoic acid. Liebermann† next showed that fuming sulphuric acid produced essentially the same effect as phosphoric pentoxide, converting the β-benzoylbenzoic acid into anthraquinone sulphoacid, and suggested that this method might be of technical value in the future. Rotering and Zincke‡ obtained a similar result by using phosphoric pentachloride, while Thörner and Zincke§ worked out the process further, and showed that chlorine acting on orthotolylphenylketone produced the same effect. Under this head might also be classed the action of hot plumbic oxide on tolylphenylketone already described in Group 2.

9. Closely related to the preceding group is the synthesis depending on the action of zinc-dust on tolylphenylketone, which was studied by Behr and Van Dorp in 1873;‖ and also in 1874,¶ when they proved that the para-compound gives no anthracene, and more recently by Ador and Rilliet.**

Finally, the occurrence of (10) anthracene among the products of the action of potassic nitrite on benzylchloride,†† and of (11) anthraquinone from the oxidation of isatropic acid,‡‡ should be mentioned.

Discovery and Syntheses of Phenanthrene.

It is highly probable that Fritzsche,§§ in 1867, encountered phenanthrene in studying the higher fractions of coal-tar with his reagent, as he describes a hydrocarbon melting near 100°; this observation was entirely overlooked, however, and we owe the first definite statements about phenanthrene to Fittig,‖‖ who announced its discovery in August, 1872; but his preliminary notice of it was so imperfect that Glaser, who discovered it at about the same time, sent it to Graebe¶¶ for investigation as a new hydrocarbon. In 1873 three independent tolerably complete accounts of it appeared

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* Ber. d. ch. G. 1874, 578. † Ibid. 805. ‡ Ibid. 1876, 631. § Ibid. 1877, 1477.
‖ Ibid. 1873, 753. ¶ Ibid. 1874, 16. ** Ibid. 1879, 2298.
†† Brunner, Ber. d. ch. G. 1876, 1744. ‡‡ Fittig, Ber. d. ch. G. 1879, 1739.
§§ Zeitschr. für Chem. 1867, 293. ‖‖ Ber. d. ch. G. 1872, 933. ¶¶ Ibid. 968.

almost simultaneously in the *Annalen der Chemie;* these were by Fittig and Ostermayer,[*] by Graebe,[†] and by Hayduck.[‡]

In Graebe's article the synthesis of phenanthrene by passing stilbene or dibenzyl through a red-hot tube is described, whereas Dreher and Otto,[§] who tried the same experiment in 1870, before the discovery of phenanthrene, naturally overlooked it.

In the following year Graebe[‖] added toluol to the substances which form phenanthrene under these conditions; and Barbier[¶] announced that Fritzsche's phosene (see page 384) was a mixture of anthracene and phenanthrene, since he succeeded in getting the characteristic test, brown plates, with Fritzsche's reagent (dinitroanthraquinone) from such a mixture. Armed with this test, he then proceeded to examine the anthracenes from various syntheses, and found phenanthrene in those made by the action of heat on styrol and benzol, ethylene and benzol, benzyltoluol, phenylxylol, and diphenylmethane; also in the anthracene made from benzylchloride by heating with water, and in that from natural alizarine by reduction with zinc-dust; as in all these cases the phenanthrene could not be detected by any other test except Fritzsche's reagent, there seems good reason for receiving these results with caution, especially as he himself has proved by direct experiment[**] that anthracene cannot be converted into phenanthrene by heat. By passing a mixture of ethylene and diphenyl through a red-hot porcelain tube, however, he obtained a large quantity of phenanthrene, and also by heating liquid ditolyl or stilbene to dull redness in a sealed tube. Finally, Kramers[††] found a trace of phenanthrene among the products from passing phenol through a yellow-hot tube.

Constitution of Anthracene and Phenanthrene.

Dumas and Laurent, in their first article on anthracene, considered it a polymerized naphthalene. Anderson, after establishing the formula, called attention to the fact that anthracene and anthraquinone differed from stilbene and benzyl only by two atoms of hydrogen in each case. Berthelot, in 1867, on account of its formation from toluol at a red heat, gave it the formula $C_6H_4[C_6H_4C_2H_2]$,[‡‡] which he showed later in the same year was supported also by Limpricht's synthesis, and his own decompositions of anthracene[§§] with hydri-

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[*] Ann. Chem. Pharm. 166, 361.

[†] Ibid. 167, 131.

[‡] Ibid. 167, 177.

[§] Ibid. 154, 176.

[‖] Ber. d. ch. G. 1874, 48.

[¶] Comptes rendus, 79, 121, 660, 810; Ann. Chim. Phys. ser. 5, 7, 515.

[**] Ann. Chim. Phys. ser. 5, 7, 515.

[††] Ann. Chem. Pharm. 189, 132.

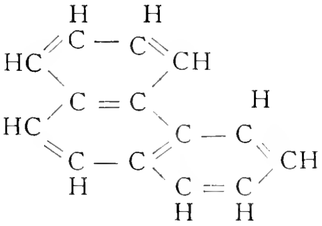
[‡‡] Calculated to modern atomic weights.

[§§] Bull Chem. Soc. 9, 295.

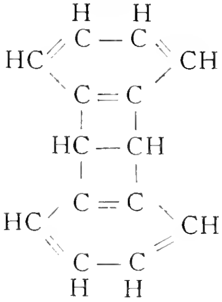
odic acid; he considered it an "acetylodiphenylene," but pointed out the fact that, while the calculated boiling-point of this substance should be 310°–320°, the boiling-point of anthracene is in reality 360°.

In 1870, Graebe and Liebermann proposed two formulas for anthracene, giving the preference to No. 1, on the ground of the syntheses

No. 1.



No. 2.



by Limpricht from benzylchloride, and Berthelot from styrol and benzol; also because this formula is like that of naphthalene, which they show is allied to anthracene in many respects; but these arguments were overturned in 1872 by the discovery of phenanthrene, which not only resembled naphthalene more closely than anthracene did, but yielded diphenic acid and other undoubted derivatives of diphenyl, and was therefore entitled to the first formula, leaving the second for anthracene. This arrangement of the formulas was confirmed by Van Dorp's synthesis of anthracene from benzyltoluol, and by some experiments by Graebe,[*] which showed that phenanthrenequinone gave diphenyl on distillation with soda-lime, while anthraquinone gave benzol and a very little diphenyl, indicating that there is no direct union of the rings in the latter.

Finally the syntheses from phthalic acid, and the formation of phthalic acid by oxidation, or the action of sulphuric acid[†] on anthraquinone, established without doubt the ortho position of the connecting atoms of carbon in one of the benzol-rings of anthracene, which was still further confirmed by the syntheses from liquid benzyltoluol and β-benzoylbenzoic acid.

At the end of 1873, therefore, the second formula had been universally adopted as that of anthracene, although the position of the

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[*] Ber. d. ch. G. 1873, 63.

[†] Weith and Bindschedler, Ber. d. ch. G. 1874, 1106.

two connecting atoms of carbon in one of the benzol-rings had not been determined, and the researches of following years, while confirming the points already established, threw no more light on this subject.[*]

With phenanthrene the case is different, as the proof of the ortho position of the two additional atoms of carbon has not been neglected. In 1878 Schmitz[†] argued that this was probably the constitution from the fact that diphenyleneketone and diphenylcarboxylic acid were completely destroyed by oxidation; while somewhat later in the same year the point was proved by Schultz,[‡] and by Anschütz and Japp,[§] almost simultaneously. Schultz did this by converting Griess's metadiamidodiphenic[||] acid (made by the reduction of metanitrobenzoic acid with tin and hydrochloric acid) into diioddiphenic acid, and reducing this to a diphenic acid, which he proved was identical with that from phenanthrene (a proof which he did not make perfectly satisfactory till a later paper,[¶] in 1879). Anschütz and Japp oxidized the sodic salt of the phenanthrenesulphoacid with potassic permanganate, and obtained phthalic acid as the only product, whereas, if phenanthrene were not a diortho compound, isophthalic or terephthalic acid must also have been formed.

In 1879 Merz and Weith[**] proposed a new formula for phenanthrene, $C_6H_4=\overset{H}{C}-\overset{H}{C}=C_6H_4$, founded on the fact that they obtained invariably perchlorbenzol instead of perchlordiphenyl by the exhaustive action of chlorine upon it; the formation of diphenic acid would then be due to an atomic transformation during the process of oxidation. This hypothesis, however, can hardly be considered as throwing doubt on the constitution of phenanthrene until supported by additional facts, especially since Japp[††] has shown by the formation and properties of the β-phenanthrenecarboxylic acid that the C_2H_2 group behaves as if it were part of a benzol ring.

At present, then, the constitution of phenanthrene must be considered as settled, while it still remains to prove the position of the two connecting atoms of carbon on one of the benzol rings in anthracene.

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[*] Anschutz (Ber. d. ch. G. 1878, 1213) made diphenyleneketone by heating anthraquinone with calcic oxide, but proves in the same paper that this reaction cannot be used as an argument in regard to the position of the C_2H_2 group in anthracene.

[†] Ann. Chem. Pharm. 193, 115.

[‡] Ann. Chem. Pharm. 196, 1. Ber. d. ch. G. 1878, 215.

[§] Ber. d. ch. G. 1878, 211.

[||] Ibid. 1874, 1609.

[¶] Ibid. 1879, 235.

[**] Ibid. 677.

[††] Ibid. 1880, 573.

Action of Sodium on Orthobrombenzylbromide.

In the hope of settling the constitution of anthracene we have studied the action of sodium on orthobrombenzylbromide, since this might lead to the formation of a hydride of anthracene by the union of two molecules, the side-chain of each being joined to the ring of the other, and of phenanthrenedihydride if the two side-chains and the two rings were united. As these two reactions were likely to take place side by side, we expected that our product would consist of a mixture of these two hydrocarbons.

Orthobrombenzylbromide dissolved in anhydrous ether[*] was warmed with sodium for some days, fresh shavings of sodium or sodium shot[†] being added from time to time, until the bright surfaces were no longer tarnished. The greater part of the sodium was then removed, and, after treatment with dilute alcohol to destroy the remainder, the product of the reaction thoroughly washed with water; the yellowish viscous mass thus obtained was oxidized with chromic anhydride, and upon subliming the product, after removing the portions soluble in water and sodic hydrate, yellow needles were obtained which melted at 273°, and gave with zinc dust and sodic hydrate a red color; they were therefore *anthraquinone.*

0.5745 gr. of the substance gave on combustion 1.7000 grs. CO_2 and 0.2180 gr. H_2O.

	Calculated for $C_{14}H_8O_2$.	Found.
Carbon	80.75	80.67
Hydrogen	3.84	4.21

The anthraquinone was further converted into the bromine compound, which by fusion with potassic hydrate yielded alizarine.[‡]

A second portion of the orthobrombenzylbromide treated with sodium, and afterward freed from it in the same way, was distilled with steam for a long time, a white substance passed over solidifying in part in the condenser, which was proved to be dibenzyl by its odor, its melting-point 52°, and the following analysis:

0.2435 gr. of the substance gave on combustion with $PbCrO_4$[§] 0.8240 gr. CO_2 and 0.1700 gr. H_2O.

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[*] When toluol was used in place of ether, the reaction ran so slowly that even after boiling for several days the sodium was but little affected.

[†] The sodium shot was made by melting sodium under toluol, and shaking (Wislicenus, Ann. Chem. Pharm. 186, 212). It seemed to be not so effective as thin shavings of sodium.

[‡] A preliminary notice of the work up to this point was published, Ber. d. ch. G. 1879, 1965.

[§] Owing to the ease with which the substance sublimes, great difficulty was encountered in getting a satisfactory combustion.

	Calculated for $C_{14}H_{14}$.	Found.
Carbon	92.31	92.27
Hydrogen	7.69	7.75
	100.00	100.02

No anthracenedihydride could be found in the distillate with steam, although it was carefully searched for.

The residue left in the flask, after the distillation with steam, was a yellow viscous mass, which can be most conveniently purified after distillation *per se*, as this destroys the greater part of the viscous substances containing bromine, which render the extraction with a solvent toilsome and unsatisfactory. The distillate, which passed over without a pause from 260° to redness, consisted of a solid mixed with oil, and had a very disagreeable rank smell, different from that of the undistilled substance. The less volatile parts of the distillate were easily converted by washing with alcohol and ether into white plates with a blue fluorescence, which melted at 212°, and were therefore *anthracene*. The residue left by evaporation of the alcoholic washings consisted of dibenzyl, a brown viscous substance containing bromine and a small amount of a yellow oil; it was tested for phenanthrene by oxidation with chromic anhydride in glacial acetic acid solution, and treatment of the product, after it had been freed from chromic compounds with water, and from acids by weak sodic hydrate, with warm acid sodic sulphite; the solution thus formed was filtered, acidified with hydrochloric (better nitric) acid, and allowed to stand for some time, when it deposited a yellow precipitate, which melted at 198°, and was therefore *phenanthrenequinone*. For further confirmation it was tested, according to Laubenheimer,* as follows: a little of the substance was dissolved in about 5 cc. of glacial acetic acid, a few drops of toluol, and 8–10 drops of sulphuric acid were added, and the mixture allowed to stand over night. It was then poured into water, which, shaken with ether, imparted to it a deep claret-red color, exactly like that obtained from pure phenanthrenequinone under the same conditions.

In a third experiment 20 grams of orthobrombenzylbromide were treated with sodium for nearly a month in the way already described, but, instead of adding water at once to the product, the organic matter was extracted from the sodium and sodic bromide

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* Ber. d. ch. G. 1875, 224.

as far as possible with ether and benzol, in order to avoid the reducing action of the hydrogen set free by water. The residue insoluble in these solvents was finally treated with water, and the small amount of organic matter thus obtained added to that at first extracted. The amount of dibenzyl in this product was notably smaller than in those which had been treated directly with water. In a weighed portion an attempt was made to determine the amount of phenanthrene, by adding picric acid to a strong alcoholic solution, but no crystals of the picric acid compound of phenanthrene separated; the solution was therefore evaporated, and in this way a few red crystals were obtained, which had the form of the compound of anthracene with picric acid, and melted in the crude state near 168° instead of at 170°; the quantity was too small to admit of purification. The formation of the anthracene compound, which is decomposed by alcohol, apparently from an alcoholic solution, can be explained by the supposition that it was not formed until the alcohol had evaporated, leaving the anthracene and picric acid dissolved in the oily impurities. In point of fact, it was obtained by imitating the above conditions; that is, evaporating an alcoholic solution of anthracene and picric acid, to which a few drops of toluol had been added. The experiment would seem to show that phenanthrene as such does not exist in the original product.

To meet the objection which might be urged, that the anthracene obtained in the second experiment was not formed directly by the action of sodium on the orthobrombenzylbromide, but during the distillation of the viscous mass, which resembled the substance obtained by Zincke both from his reaction and the action of water at high temperatures on benzylchloride, another portion was treated with ether and hot alcohol, which removed a yellow oil and left *anthracene* identified by crystallizing in white plates melting at 210°. The yellow oil contained either phenanthrene or its dihydride,* as it gave phenanthrenequinone by oxidation, but we were unable to determine which of these substances was present on account of the small amount at our disposal. We are therefore in doubt as to the way in which the phenanthrene occurs in our product; for, on the one hand, we could not obtain the picric acid compound either from the original product or the yellow oil, while, on the other, a substance crystallizing in plates melting between 170° and 190°,

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* Phenanthrenedihydride has never been prepared with certainty, although Barbier (Comptes rendus, 79, 121) thought it was formed by the reduction of phenanthrene with sodium amalgam.

which has appeared more than once in the course of this work as an intermediate product in the purification of the anthracene, yields on oxidation anthraquinone and phenanthrenequinone, and seems therefore to be a mixture of the two free hydrocarbons.

No anthracenedihydride could be found in any of the products, nor have we succeeded in detecting benzyltoluol or ditolyl, although it is highly probable that they were formed in addition to the dibenzyl; but the acids resulting from the oxidation appeared in such small quantities, and so contaminated with a brown impurity formed from the viscous brominated substance, that it was impossible to obtain any definite result from them. The viscous substances, too, containing bromine, which were the principal products of the reaction, have resisted thus far all our efforts to bring them into a form suitable for analysis, but we hope to return to this part of the subject hereafter.

Finally the following quantitative results were obtained:—

Organic product from 20 grs. orthobrombenzylbromide	10.85	grs.
Calculated product if free from bromine	7.12	"
Bromine not removed by the sodium	3.73	"
Bromine in 20 grs. orthobrombenzylbromide	12.88	"
Bromine removed as bromide of sodium	9.71	"
Bromine not removed by the sodium	3.17	"

The "bromine removed as bromide of sodium" was determined by precipitating 7.727 grs. of the wash-water with argentic nitrate, which gave 1.482 grs. of argentic bromide. As the weight of the wash-water was 119 grs. this corresponds to the result given above. The two determinations of the amount of bromine not removed by the sodium agree as closely as could be expected when the losses resulting from the repeated extraction and washing of the viscous organic products are taken into account.

75.4 per cent of the whole amount of bromine contained in the orthobrombenzylbromide was therefore removed by the sodium.

Determination of the Amount of Anthracene by Luck's[*] *Method.* —1.04 grs. of the product, oxidized, first with chromic anhydride dissolved in glacial acetic acid, and afterward with an alkaline solution of potassic permanganate, gave 0.158 gr. of anthraquinone,

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[*] Zeitschr. Anal. Chem. 1873, 347; 1874, 251.

corresponding to 0.135 gr. of anthracene, that is, 1.409 grs. from the 20 grs. of orthobrombenzylbromide used, or 19.78 per cent. of the theoretical yield.

Determination of the Amount of Phenanthrene.—2.44 grs. of the original product, oxidized carefully by adding a strong aqueous solution of chromic anhydride to a hot solution of the substance in glacial acetic acid as long as a drop of the oxidizing agent made the liquid boil,* on extraction of the product with acid sodic sulphite and acidification with nitric acid, yielded 0.05 gr. of phenanthrenequinone, which corresponds to 0.0428 gr. of phenanthrene; that is, from 20 grs. of orthobrombenzylbromide 0.190 gr., or 2.66 per cent. of the theory. The amount of phenanthrene actually formed must have been somewhat larger than this, as some of the quinone was undoubtedly destroyed by the chromic anhydride,—in fact, the operation can hardly be called a quantitative one.

From the work described above, it appears that 20 grs. of orthobrombenzylbromide yielded,—

Total organic product	10.850	grs.
Anthracene	1.409	"
	9.441	"
Phenanthrene	0.190	"
	9.251	"
Dibromdibenzyl, or its isomeres, calculated from 3.17 grs. of unremoved bromine	6.738	"
Undetermined, containing phenanthrene, dibenzyl, benzyltoluol, and ditolyl	2.513	"

Summary of Results.

Orthobrombenzylbromide when treated with sodium yields anthracene (identified by its melting-point 212°, the formation of anthraquinone melting-point 273°, and of alizarine; 19.78 per cent. of the theoretical yield); and phenanthrene (identified by the melting-point of its quinone 198°, and by Laubenheimer's test; 2.66 per cent. of the theoretical yield). Certainly part, and probably all, of the anthracene occurs in the free state; no anthracenedihydride could be found. Our experiments leave us in doubt as to the way

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* Liebermann and Hörmann, Ber. d. ch. G. 1879, 591.

in which the phenanthrene occurs. Dibenzyl was also obtained, an oil possibly benzyltoluol or ditolyl, and a viscous substance containing bromine.

By this synthesis of *anthracene* from orthobrombenzylbromide, it is proved that the *two connecting carbon atoms are attached to each ring in the ortho position*, and thus the last doubt about the constitution of anthracene is removed.

The synthesis of phenanthrene, while it confirms the ortho attachment of the two additional atoms of carbon, proves nothing either for or against the formula recently proposed by Merz and Weith.

The publication of the preliminary notice of this work, already mentioned, drew out an article from Von Pechmann,* describing work done at about the same time as ours, in which he applies to anthracene the ingenious method contrived by Graebe for determining the constitution of naphthalene as follows: bromorthobenzoylbenzoic acid, prepared by the action of bromphthalic acid on benzol in presence of aluminic chloride, was converted into bromanthraquinone by heating with sulphuric acid, which on fusion with potassic hydrate gave erythroxyanthraquinone, and, as this when oxidized yielded phthalic acid, the conclusion drawn from our experiments that anthracene is a diortho substance is confirmed by his work.

CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE COLLEGE.

VIII.—ON SAUER'S METHOD OF ESTIMATING SULPHUR, AND SOME MODIFICATIONS.

By W. G. Mixter.

Several years ago, A. Sauer† and the writer‡ proposed methods for determining sulphur in coals and organic compounds by burning in oxygen and oxidizing the sulphur dioxide with bromine.

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* Ber. d. ch. G. 1879, 2124. † Fres. Zeit. 12, 32. ‡ Am. Jour. Sci. & Arts, 3d series, 4, 90.

The former passed the products of combustion through two U tubes containing a hydrochloric acid solution of bromine, and the latter burned in a confined volume of moist oxygen and a little bromine vapor. The writer stated that experiments made by passing the products of combustion of sulphur compounds through nitric acid failed to give satisfactory results. A variable loss was due to a dense white fume containing sulphuric acid, which was not completely absorbed by water or by caustic alkalies. It was mentioned that the apparatus employed was designed to avoid this source of error.

With the hope that Sauer's method or some simple modification of it would give satisfactory results, the following experiments have been made. For the burning of volatile substances, Sauer's plan of a doubly perforated rubber stopper in the anterior end of the combustion tube did not seem desirable, as some sulphuric acid is liable to condense with the water against this stopper; or in case little water is present, some strong sulphuric acid may come in contact with the rubber; hence oxygen was passed through the small hard glass tube *a*, fig. 1, to *c*. Carbonic acid or air was passed in very slowly through *b* during the volatilization of the assay to prevent the condensation in the cold anterior end of the combustion tube. After all volatile matters had burned, the rubber tubes, connecting with the oxygen and carbonic acid supplies, were closed by clamps and reversed, so that on opening the clamps oxygen passed through *b*, and a very slow current of carbonic acid through *a*. The products of combustion were passed through two U tubes, such as figured by Sauer, containing a solution of bromine in a mixture of one part of fuming hydrochloric acid and two parts of water. In order to find whether the cloud which issues from the U tubes contains sulphur, it was passed by means of a glass tube to near the bottom of an eight-litre bottle. This cloud or fume usually has a well defined surface, which seldom rises above the middle of the bottle. After the cloud completely subsided, the bottle was rinsed three times with water, and the sulphur was precipitated as barium

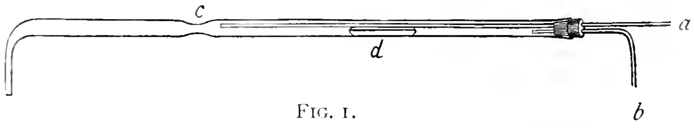

FIG. 1.

sulphate. Sauer's plan for non-volatile substance was tried, with the addition of the large bottle above described. In all the experiments the rinsings of the combustion tube were added to the solutions from the U tubes.

	I.	II.
Pure sulphur taken	0.2010	0.2638
Total sulphur found	99.69 per cent.	99.85 per cent.
Sulphur found in bottle	0.89 "	0.25 "
Time of burning	1 hour.	15 minutes.

About four times as much oxygen and carbonic acid were used in I as in II.

	I.	II.
Coke	2	2 grams.
Total sulphur found in gaseous products	0.79 per cent.	0.78 per cent.
Sulphur found in bottle	0.13 "	1.17 "

In order to find whether there is any loss of sulphur in estimating it by this method in substances like coke, a mixture of sugar charcoal and pyrite, FeS_2, containing a known amount of sulphur,* was tried.

	I.		II.	
Charcoal	2	grams.	2	grams.
Pyrite	0.2258	"	0.2057	"
Sulphur calculated	0.1199	"	0.1092	"
Total sulphur found	0.1198	"	0.1091	"
Sulphur found in bottle	0.0131	"	0.0099	"

The results show that in I, 99.91, and in II, 99.90 per cent. was found of the sulphur taken, and that 11 per cent. in I and 9 per cent. in II passed into the large bottle. No sulphur was found in the residue in the tray. The time of the actual burning of each of the assays was about three-quarters of an hour.

In the two following experiments the products of combustion were passed through 75 cc. of fuming hydrochloric acid, saturated with bromine, distributed in three bulbs of an absorbing apparatus, each

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* The pyrite was treated with cold nitric acid, and the whole was kept cool in water, and by constant agitation until only finely divided sulphur remained. On heating in a water-bath the sulphur disappeared and a complete solution resulted. The excess of acid was evaporated, the sulphur was precipitated as $BaSO_4$, the precipitate was fused with sodium carbonate. The fused mass was washed and the sulphur was reprecipitated in the acidified filtrate.

	I.	II.	
Pyrite taken	0.3230	0.3165	mean.
Per cent. sulphur found	53.14	53.08	53.11

bulb having a capacity of 200 cc., and so arranged that the gases bubbled through the liquid in each bulb and finally passed into the large bottle. The apparatus was made entirely of glass to avoid any question of sulphur from rubber connections. The burning in each test occupied about three-quarters of an hour. The results show that about two parts in one hundred parts of sulphur used were not absorbed by the bromine solution.

Charcoal	2	2	grams.
Pyrite	0.2058	0.219	"
Sulphur found in bottle . . .	0.0018	0.0023	"

A hydrochloric acid solution of bromine is probably a no better absorbent of sulphur dioxide than bromine water, and is objectionable for the reason that the excess of hydrochloric acid must be evaporated so that some barium sulphate may not remain dissolved. Bromine water with a cubic centimetre or two of undissolved bromine, in a common two-bulb U tube, loses bromine rapidly when gas bubbles through it, but when the liquid bromine mixes gradually with the water, the passing gas removes the bromine slowly. In the two following experiments, a four-bulb U tube with two bulbs on the bottom was used. Two cubic centimetres of bromine were placed in the lower bulb next to the combustion tube, and sufficient water was added to trap three of the bulbs. It was necessary to shake the U tube occasionally during the combustion in order to keep bromine distributed through the water. The large bottle was used as before. A trace of sulphur found in the residues in the tray was weighed with the total sulphur. The time of actual burning was about three-quarters of an hour.

	I.	II.	
Charcoal	2	2	grams.
Pyrite	0.2024	0.2087	"
Sulphur calculated	0.1075	0.1108	"
Total sulphur found	0.1071	0.1108	"
Sulphur found in bottle	0.0062	0.0026	"

These figures show that 99.63 and 100 per cent. of the total sulphur taken was found, and that 5.77 and 2.35 per cent. respectively condensed in the large bottle, and also that bromine water may replace a hydrochloric acid solution of bromine.

After experimenting with various forms of U tubes, designed for keeping bromine distributed through the water during the passage of the gases from the combustion, the bulb tube *A*, shown in fig. 2, was found suitable for this purpose. It is about 30 cm. long and 20 cm. high, and is narrowed at the necks so that small rubber stoppers may be used. The enlarged part represents the full size of this portion of *A*. The slight elevation in the glass at *d* is to keep the liquid bromine, shown at *f*, from passing into the narrowed part *e*. A description of the manner of using this absorbing tube will make clear the reasons for the shape at *d* and *e*. It is first connected with the combustion tube *c*, and a cubic centimetre of bromine is poured in and then water added to fill it to the bulbs and the narrow glass tube *g* is adjusted. This tube *g* dips under a little water in *B*. *A* is then slightly inclined so that bubbles of gas from the combustion may slowly pass the lower limb. From time to time, as bromine disappears from the surface of the water, *A* may be inclined more so that a drop or two of bromine shall enter the narrow part *e*, where the passing gas mixes it thoroughly with the water. The remaining experiments were made in the apparatus above described, and the form of combustion tube shown in fig. 1.

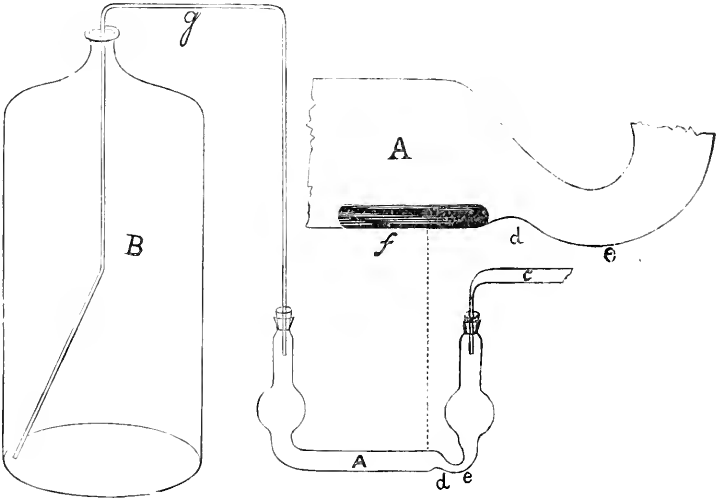

FIG. 2.

	I.	II.	
Sugar	0.670	1	gram.
Sulphur	0.2028	0.2777	"
Sulphur found	0.199	0.2747	"
Per cent. of Sulphur found . .	98.12	98.95	

In I. a slight deposit of unburned matter remained in the bend of the combustion tube.

0.2783 gram of pure carbon disulphide yielded 83.53 per cent. of sulphur; theory requires 84.20. In another trial with carbon disulphide, free sulphur was found in the bromine water.

The first trial with cannel coal was a failure, owing to too rapid volatilization. A light-colored sticky substance containing carbon and a trace of sulphur was found in the bottle *B*. In a second experiment the combustion appeared to have been complete, and 3.1 per cent. of sulphur was found in the volatile portion of the coal.

The results obtained show that Sauer's method is good if the sulphur which passes the bromine solution is caught in a large bottle. A much smaller bottle than the one used would probably stop all the sulphur, but an eight-litre bottle does not allow a troublesome amount of bromine to escape into the room: 150 cc. of water are sufficient to rinse the bottle. Complete combustion can be insured by volatilizing so slowly that the flame of the burning vapors remains a few millimetres back of the end of the tube delivering oxygen. Sauer's apparatus as modified by the writer, supposing a combustion furnace and gas-holders are at hand, has the advantage of simplicity and fewer connections over the plan proposed by the writer for burning in a confined space. Sauer's method requires double to treble the time for burning, and with volatile substances more care to insure complete burning than the writer's original method.

THE DETERMINATION OF SULPHUR IN SULPHIDES AND IN COAL AND COKE.*

BY THOMAS M. DROWN.

The use of bromine as an oxidizing agent, particularly for sulphur, has become very general in analysis, replacing the stronger oxidizing acids. The object of this paper is to describe briefly the experience which we have gained with this reagent in the laboratory of Lafayette College in the oxidation of metallic sulphides.

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* Read before the American Institute for Mining Engineers.

Most of the simple sulphides, as blende, pyrite, etc., when exposed to the combined action of an alkaline hydrate and bromine, and finally to hydrochloric acid, are completely and promptly dissolved. The procedure is as follows: The very finely pulverized mineral is first treated, in a beaker, with a solution of sodium hydrate of a specific gravity of 1.25, and heated; bromine is then cautiously added to supersaturation, and finally hydrochloric acid to acid reaction. If any of the sulphide is not taken up, the same operation may be repeated. It is necessary, however, that the mineral be very finely pulverized. Instead of using the pure bromine, a saturated solution of bromine in potassium bromide may be used with equally good effect.

The process is advantageously simplified by making a saturated solution of bromine in the concentrated alkali. This is done by pouring bromine into a solution of sodium hydrate, of the above given specific gravity, until no more is taken up, and then adding a little of the sodium hydrate solution until the liquid does not give off free bromine. The procedure with this solution is as follows: The pulverized mineral is moistened with, say, 10 cc. of the solution, and heated, then hydrochloric acid added to just acid reaction. Two more additions of the alkaline solution, in amounts of 20 cc. each, are added at intervals of about ten minutes, each addition being followed by hydrochloric acid. The total amount of the alkaline solution (containing the bromine) used is, therefore, 50 cc., and the amount of hydrochloric acid should not exceed that necessary to make the solution acid after each addition of the alkali. The mixture should be kept hot. After the final addition of acid, the contents of the beaker is taken to dryness and heated in an air bath to 110° to 115° C., to render silica insoluble. The dry mass is then taken up by hydrochloric acid, and after filtration the sulphuric acid is precipitated by barium chloride. In a sample of copper pyrites Mr. F. E. Bachman obtained, in duplicate analyses, 34.05 and 34.12 per cent. sulphur; in zinc blende 32.97 and 33.09 per cent. In another sample of blende Mr. P. W. Shimer obtained 32.71 per cent.

This method of determining sulphur I find especially valuable in the analysis of coal. By the treatment of coal as above described results are obtained which agree very closely. The coal, as such, is not attacked, and the sulphur obtained, therefore, represents that existing in the coal as pyrite, and also as soluble sulphates. The residue left by this treatment has been subjected again to the same process, and yields no more sulphur. On combustion, however, or by complete oxidation, either by oxidizing acids or by fusion, additional sulphur may be obtained, which must represent that combined organically with the coal.

The following are some of the results obtained by Mr. Shimer from bituminous coals by the bromine method. The amount usually taken for analysis was between one and two grams:

Bituminous coals.	Total sulphur by fusion with alkaline carbonates and nitrates.	Sulphur by bromine process.
I.	0.043	0.035
		0.035
		0.035
II.	2.16	1.80
	2.17	1.81
		1.81
		1.83
		1.84
		1.85
		1.87
III.	1.17	0.710
	1.18	0.713
		0.717
IV.	1.48	1.096
	1.49	1.098
	1.50	1.100
		1.100

In comparing the bromine method with others it was found that the treatment with hydrochloric acid and potassium chlorate gave on coals with but little sulphur in the form of pyrite the same results, but on coals with much pyrite the results were decidedly lower than by the bromine method. But too few experiments were tried on this point to be decisive. The action of nitric acid and potassium chlorate depends upon the nature of the coal. Some coals are converted partly into a brown unmanageable solution, and others are oxidized completely to a clear solution. In the latter case, of course, the total sulphur could be obtained.

As was said above, the sulphur obtained by the bromine method represents both the sulphides and sulphates in the coal. The methods ordinarily given for the separate determination of calcium sulphate are faulty. Sodium carbonate readily attacks pyrite, and dilute hydrochloric acid and even water, when heated for some time in contact with pyrite, with access of air, contain notable quantities of sulphuric acid. It would seem, therefore, necessary to dissolve out the calcium sulphate by means of water with the careful exclusion of air.

The determination of the total sulphur in coal by means of fusion with alkaline carbonates and nitrates, or chlorates, I find unsatisfactory, owing, I think, to the large amount of salts in the solution in which the barium sulphate is precipitated. A much better method is to burn the coal in a platinum boat placed in a glass tube in a current of oxygen. The products of combustion may be absorbed by a solution of bromine in hydrochloric acid, or by a dilute solution of potassium permanganate. The latter, I have satisfied myself, gives equally good results with the bromine. It is absolutely necessary, in this process, as originally pointed out by Muck,* that the combustion-tube should be washed out with water after the completion of the combustion, since sulphuric anhydride condenses in considerable quantity in the tube beyond the boat. It is further necessary, of course, to fuse the residual ash with alkaline carbonates to determine the sulphur which has not been volatilized by the combustion.

I have in progress an interesting investigation on the effect of coking on the sulphur in coal, to determine what influence the nature of the sulphur—whether in combination with iron as pyrite or organically combined with the coal—has on its elimination in coking. These results must, however, be reserved for a future communication.

LAFAYETTE COLLEGE, EASTON, PA.

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* Zeitschrift analyt. Ch. 14, 16.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

VII.—SULPHOTEREPHTHALIC ACID.

BY IRA REMSEN AND W. BURNEY.

In an earlier paper entitled "Experiments in the Para-Series,"* it was shown that, when sulphamineparatoluic acid is oxidized with potassium permanganate without the addition of an alkali, the product is *sulphoterephthalic acid.* An acid potassium salt and an acid barium salt were prepared and analyzed, and some neutralization experiments were made with the potassium salt. All the results obtained proved unmistakably that the acid is really sulphoterephthalic acid. Still, in view of the unusual character of the reaction, it seemed desirable to examine the product more thoroughly, and to furnish unanswerable proofs of the correctness of the conclusion first drawn concerning it. As the acid under consideration must be tribasic, the attempt was first made to obtain salts the composition of which would prove its tribasic character. Such salts were obtained. Further, to show that the acid cannot be sulphamineterephthalic acid, the formation of which would naturally be expected as a result of the oxidation of sulphamineparatoluic acid, a new method of preparation was employed. Instead of starting from the sulphamine compounds, the sulphonic acid of cymene was itself oxidized, and sulphoterephthalic acid was readily obtained in this way. The details of the experiments are described in this paper.

In preparing sulphoterephthalic acid the directions given in the paper above referred to were closely followed. The quantities of the substances used in the oxidation of sulphamineparatoluic acid were: 15 grams of the acid, 75 grams potassium permanganate and 1500 cc. water in each flask. The mixture was heated on a water-bath for 8 to 10 hours. The acid potassium salt finally obtained corresponded closely to the description already given. After two crystallizations it proved to be pure. Several tests were made for nitrogen by fusing small quantities of the substance with sodium, but no evidence of its presence could be obtained. From a hot

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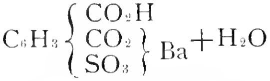
* This Journal, 2, 50.

solution of the acid potassium salt the barium salt was precipitated by means of barium chloride. The salt was well washed out on the filter, and then brought into a beaker and boiled with water, after which it was again filtered and washed. A determination of the water of crystallization of this salt was made and the results agreed with those previously found.

0.9890 gram salt lost 0.0456 gram H_2O at 300°.

This loss corresponds to 4.61 per cent. water, while the formula



$C_6H_3\left\{\begin{array}{l}CO_2H\\ \left.\begin{array}{l}CO_2\\ SO_3\end{array}\right\}Ba\end{array}\right.+H_2O$ requires 4.51 per cent. H_2O.

Neutral Barium Salt.—A weighed quantity of the above mentioned acid barium salt was placed in a flask with water and some pure barium carbonate. The flask was connected with a test-tube containing lime-water, and the contents then heated. A brisk evolution of carbon dioxide ensued, as was shown by the effervescence and the precipitation caused in the lime-water. Although these facts clearly prove that the salt with which we operated contains acid hydrogen, the solution filtered from the excess of barium carbonate did not yield a salt of constant composition. Thinking that possibly the neutral salt first formed might be decomposed by evaporation of the solution, a weighed quantity of the acid salt was boiled with barium carbonate, the liquid then filtered off, fresh water added and the fresh liquid boiled. These operations were repeated until the filtrate gave but a very slight precipitate with sulphuric acid. The united filtrates were now evaporated to a comparatively small volume, and the amount of barium contained in the liquid determined. The amount found did not, however, agree with that required for the neutral salt. In one case too little was found, in another too much.

These experiments indicate either that the neutral barium salt is very difficultly soluble in water, or that it is easily decomposed by boiling with water. Hence another method for its preparation was tried.

About two grams of the acid salt were placed in a large test-tube with a well-fitting, doubly perforated stopper. A clear, strong solution of pure barium hydroxide was then poured upon the salt, and the tube quickly corked. The salt first passes almost completely into solution, the liquid being only slightly clouded, but in a few seconds a bulky precipitate is formed, and the liquid clears up.

After standing well corked for about an hour, the barium hydroxide was washed out by passing water in through a tube reaching nearly to the bottom of the vessel containing the salt. Great precaution was taken to prevent contact with the air during the washing process. This was continued until the wash-water gave little or no precipitate with sulphuric acid. Then the salt was brought on a filter and further washed with cold water. The salt dried in the air was analyzed.

I. 0.5426 gram salt lost 0.0751 gram H_2O at 275°, and gave 0.3646 gram $BaSO_4$.

II. 0.5468 gram salt lost 0.0760 gram H_2O at 275°, and gave 0 3665 gram $BaSO_4$.

		Calculated.		Found.	
				I.	II.
$(C_8H_3O_7S)_2$	...	486	46.69	...	...
Ba_3	...	411	39.48	39.51	39.41
$8H_2O$	...	144	13.83	13.84	13.88
		1041	100.00		

The analyses show that the substance is the *neutral barium salt of sulphoterephthalic acid*, $\left\{C_6H_3\left\{\begin{matrix}CO_2\\CO_2\\SO_3\end{matrix}\right.\right\}_2 Ba_3+8H_2O$. Prepared as above described it is of distinctly crystalline appearance. It is almost entirely insoluble in cold water, and but slightly soluble in hot water.

The great insolubility of the salt explains the lack of success which attended our efforts to obtain it by boiling the acid salt with barium carbonate.

Primary barium salt, $\left\{C_6H_3\left\{\begin{matrix}CO_2H\\CO_2H\\SO_3\end{matrix}\right.\right\}_2 Ba+5H_2O$. When the secondary barium salt first obtained is treated with moderately concentrated hydrochloric acid, it dissolves with ease if gentle heat is applied. From this solution there separate on cooling well-formed crystals. These were washed once or twice with a little cold water, then again dissolved in a small quantity of hydrochloric acid, and allowed to crystallize. The crystals thus obtained were washed carefully to remove the last traces of barium chloride. The salt was dried by standing in the air and then analyzed.

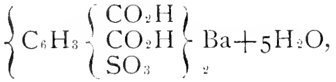
I. 0.5360 gram salt lost 0.0674 gram H_2O at 235°, and gave 0.1738 gram $BaSO_4$.

II. 0.5328 gram salt lost 0.0670 gram H_2O at 219°, and gave 0.1731 gram $BaSO_4$.

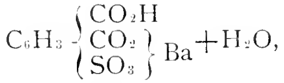
		Calculated.		Found.	
$(C_8H_5O_7S)_2$	...	490	68.34	...	...
Ba	...	137	19.11	19.07	19.10
$5H_2O$	...	90	12.55	12.57	12.57
		717	100.00		

The preparation of the three barium salts which have been described proves beyond any possibility of a question that the acid with which we are dealing is sulphoterephthalic acid.

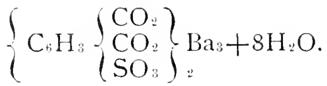
The tribasic sulphoterephthalic acid, $C_6H\left\{\begin{matrix}CO_2H\\CO_2H\\SO_3H_3\end{matrix}\right.$, obtained by oxidizing sulphamineparatoluic acid, $C_6H_3\left\{\begin{matrix}CH_3\\CO_2H\\SO_2NH_2\end{matrix}\right.$, yields the three distinct, well characterized barium salts:

Primary salt 

$$\left\{C_6H_3\left\{\begin{matrix}CO_2H\\CO_2H\\SO_3\end{matrix}\right\}\right\}_2 Ba+5H_2O,$$

Secondary salt 

$$C_6H_3\left\{\begin{matrix}CO_2H\\ \left.\begin{matrix}CO_2\\SO_3\end{matrix}\right\} Ba\end{matrix}\right. +H_2O,$$

Tertiary salt 

$$\left\{C_6H_3\left\{\begin{matrix}CO_2\\CO_2\\SO_3\end{matrix}\right\}\right\}_2 Ba_3+8H_2O.$$

For some reason unknown to us the experiments with the potassium salts were not as successful as those with the barium salts.

Neutral potassium salt, $C_6H_3\left\{\begin{matrix}CO_2K\\CO_2K\\SO_3K\end{matrix}\right.$. A quantity of the primary potassium salt, $C_6H_3(CO_2H)_2SO_3K+H_2O$, was dissolved in water and exactly neutralized by means of a solution of potassium carbonate. The solution thus obtained was evaporated to dryness, as several attempts to obtain it in crystallized form gave unsatisfactory results. The salt thus obtained is very easily soluble in water. From very concentrated solutions it separates in the form of white, verrucous masses.

Although the results of the analysis of this salt are not good, they nevertheless show that it is the neutral potassium salt of sulphoterephthalic acid.

0.4675 gram salt gave 0.3296 gram K_2SO_4. This corresponds to 31.61 per cent. K, while the dry neutral salt requires 32.56 per cent. K.

In order to obtain the secondary potassium salt, $C_6H_3\left\{\begin{array}{l}CO_2H\\ CO_2K,\\ SO_3K\end{array}\right.$ a solution of the primary salt was divided into two equal portions. One of the halves was then neutralized with potassium carbonate, and the second half added after the neutralization. On evaporation, the solution, strange to say, yielded a product which proved to be a mixture of the primary and another salt, from which it could not be separated. The first crop of crystals being analyzed, gave results about midway between those required for the primary and for the secondary salts. Thus in one case the dried salt gave 18.62 per cent. K, while the secondary salt requires 24.2 per cent. K and the primary salt 13.8 per cent. K.

Another attempt to prepare the secondary salt proved equally unsuccessful. A weighed quantity of the primary salt was brought into solution, and the exact quantity of potassium carbonate necessary to produce the secondary salt then added. On evaporating the solution thus obtained, the salt which separated was found not to have a uniform composition, and the results of the analyses agreed with none of those required by the three possible salts. The product had, further, the appearance of being a mixture apparently of two salts, one crystallized in well-formed crystals, the other being at best but crystalline. It would appear from these experiments that, while the primary and tertiary potassium salts are stable compounds, the secondary salt cannot exist. It is difficult to see how the primary and tertiary salts can exist independently in the same solution and crystallize out at the same time, yet it appears that this actually does take place. Be this as it may, the existence of the tertiary salt above described furnishes the desired proof of the tribasic character of the acid under consideration.

Action of Phosphorus Pentachloride and Ammonia on Sulphoterephthalic Acid.

In other papers it has been shown that, when phosphorus pentachloride and ammonia are allowed to act successively on compounds containing a carboxyl and a sulpho-group in the ortho-position with reference to each other, the product does not contain two amide groups, but belongs to the class of bodies which have been designated as *sulphinides*, and of which benzoic sulphinide, $C_6H_4\left\{\begin{array}{l}SO_2NH\\ CO\lrcorner\end{array}\right.$, obtained from orthosulphobenzoic acid, is the simplest example. On treating the dry potassium salt of sulphoterephthalic acid in the manner mentioned, the reactions were found to take place as usual, and a substance was formed which crystallizes in long delicate needles from water. It is difficultly soluble in cold water, more easily in hot. After one crystallization it was found to be pure, and was then subjected to analysis.

I. 0.2880 gram substance gave 32.4 cc. N under 764.4 mm. pressure and at 23°.

II. 0.3566 gram substance gave 0.3669 gram $BaSO_4$.

	Calculated for $C_6H_3\left\{\begin{array}{l}SO_2NH\\ CO\lrcorner\\ CONH_2\end{array}\right.$	Found.
N	12.39 per cent.	12.76
S	14.16 "	14.13

These results show that the reaction takes place in a manner analogous to that previously noticed in similar cases in this laboratory. The product instead of being the normal amide of sulphoterephthalic acid, viz., $C_6H_3\left\{\begin{array}{l}SO_2NH_2\\ CONH_2\\ CONH_2\end{array}\right.$, is a condensation product of the formula $C_6H_3\left\{\begin{array}{l}SO_2NH\\ CO\lrcorner\\ CONH_2\end{array}\right.$. It is the *amide of sulphinidoterephthalic acid.*

Formation of Sulphoterephthalic Acid by Oxidation of Cymenesulphonic Acid.

Any doubt concerning the nature of the substance, which we have called sulphoterephthalic acid, that may arise in consequence of the fact that the acid is a product of the oxidation of a nitrogenous substance, is removed, when we consider another and simpler method of preparation which does not involve the use of a nitrogenous substance. We succeeded after some failures in obtaining sulphoterephthalic acid by direct oxidation of cymenesulphonic acid. We first endeavored to effect the oxidation by means of chromic acid. For this purpose eleven grams of potassium cymenesulphonate were treated with the usual chromic acid oxidizing mixture. As soon as the temperature of the water-bath in which the flask stood reached 60-70° the reaction began. The flame was then removed, the action continuing, as seen by brisk effervescence of the liquid. As the action became less marked, gentle heat was again applied, and in about an hour more the liquid was heated to boiling over a free flame for three hours. In order to reduce the excess of the chromic acid a little alcohol was added. The mass was then diluted to several times its volume with water, and treated with chalk until neutral. The lime was precipitated exactly from the solution thus obtained by means of a solution of potassium carbonate; the filtrate was evaporated to dryness, acidified with sulphuric acid and extracted with alcohol. A small quantity of an organic potassium salt was finally obtained which crystallized in the form of short needles. This was analyzed with the results here recorded:

I. 0.4308 gram substance lost 0.0522 gram H_2O at 75°, and 0.0535 gram at 280°; and gave 0.1282 gram K_2SO_4.

It will be seen that the water is nearly all given off at 75°, though there is a slight additional loss if the heating is carried above this point to 280°, as it was in our analysis. If we take the result at 280° as representing the water of crystallization, the figures obtained correspond very well with those required for the formula

$$C_6H_3\begin{cases}CH_3\\COOH\\SO_3OK\end{cases} + 2H_2O.$$

	Calculated.	Found.
K	13.48 per cent.	13.36 per cent.
H_2O	12.41 "	12.42 "

A sulphotoluic acid has been obtained by Flesch[*] in the course of an investigation on the sulphur derivatives of cymene. He obtained it by oxidizing cymenesulphydrate with nitric acid, the HS group being converted into the sulpho-group, and the methyl group into carboxyl. As the acid thus obtained when fused with potassium hydroxide yields an oxytoluic acid identical with that described by von Gerichten[†] and by Remsen and Hall,[‡] and

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[*] Berichte d. deutsch. chem. Gesell. 6, 481. [†] Ibid. 11, 1586. [‡] This Journal, 2, 54.

which has been called α-oxyparatoluic acid, it follows that the sulphotoluic acid of Flesch must be identical with that formed by direct oxidation of cymenesulphonic acid, assuming that the oxidation of the latter acid takes place in the same way as that of cymenesulphamide. Flesch states that the acid potassium salt of his acid contained three molecules of water of crystallization. The corresponding salt of our acid was found to contain only two molecules of water. It is possible that some water may have been given off by simple exposure to the air, as that which was determined was given off very easily at the low temperature of 75°.

It is thus seen that the oxidation of cymenesulphonic by means of potassium pyrochromate takes place as the earlier experiments would lead us to expect. The effect of the oxidation is confined mainly, if not entirely, to the propyl group, the methyl group being protected.

In order to effect the oxidation of the methyl group of sulphotoluic acid, potassium permanganate was used. The acid potassium salt obtained by the oxidation with chromic acid, purified as well as possible by means of crystallization, was dissolved in 400 cc. of water and then nearly neutralized by potassium carbonate, the free acid having been found to interfere with the oxidizing action of the permanganate. A solution of permanganate was then prepared containing 30 grams of the salt in 200 cc. water. One-third of this solution was added to the solution of the sulphotoluate, and the whole heated on the water-bath for about three-quarters of an hour, when it was found to be completely decolorized. 33.3 cc. of the permanganate solution were now added, and the heating continued for an hour and a half to two hours. As no further decolorization of the permanganate took place, the process was stopped and the slight excess of permanganate reduced by means of a little alcohol. The filtered solution was evaporated down to a small volume, allowed to cool and then acidified with hydrochloric acid. A large crystalline precipitate was formed. This was collected and recrystallized, when it was seen to have the same appearance as the acid potassium sulphoterephthalate obtained from sulphamineparatoluic acid. It was analyzed with these results:

I. 0.5339 gram lost 0.0335 gram H_2O at 150°, and gave 0.1533 gram K_2SO_4.

II. 0.5536 gram lost 0.0333 gram H_2O at 150°, and gave 0.1594 gram K_2SO_4.

		Calculated.		Found.	
				I.	II.
$C_8H_5O_7S$	...	245	81.10	...	...
K	...	39.1	12.94	12.89	12.92
H_2O	...	18	5.96	6.27	6.01

The physical properties of the salt taken together with the results of the analyses show conclusively that it is identical with monopotassium sulphoterephthalate. A further proof of the identity is given in the fact that when the solution of the salt is treated with barium chloride, a crystalline barium salt is precipitated which conducts itself exactly like barium sulphoterephthalate already described. And on analysis it was found to have the same composition.

0.5477 gram lost 0.0269 gram H_2O at 300°, and gave 0.3177 gram $BaSO_4$.

		Calculated.		Found.
$C_8H_4O_7S$	...	244	61.15	....
Ba	...	137	34.34	34.11
H_2O	...	18	4.51	4.91

It can then scarcely be doubted that the product obtained by the oxidation of sulphamineparatoluic acid with potassium permanganate in neutral solution, and which has been declared by Remsen and Hall to be sulphoterephthalic acid, is identical with the oxidation-product of sulphotoluic acid, and, as the presence of nitrogen in the latter product is an impossibility, it will, we think, scarcely be claimed in the future that both products of oxidation of sulphamineparatoluic acid contain nitrogen. Of the two methods given for the preparation of sulphoterephthalic acid probably that involving the use of the sulphonic acid of cymene will be found to be the better. Judging from our results there should be no difficulty in preparing the acid in any desired quantity.

VIII.—SULPHOTEREPHTHALIC ACID FROM PARAXYLENE-SULPHONIC ACID.

By Ira Remsen and M. Kuhara.

In view of the results described in the preceding paper, it seemed desirable to complete the chain of evidence concerning the nature of the acid under consideration by preparing it from the sulphonic acid of paraxylene. Pure paraxylene was prepared synthetically from parabromtoluene and methyl iodide according to the well-known method. On distillation the hydrocarbon solidified in the condensing tube. The pure hydrocarbon was converted into the sulphonic acid by mixing it with an equal volume of fuming sulphuric acid. The hydrocarbon dissolved easily with elevation of temperature. The solution was diluted with water, neutralized with chalk, and filtered. The potassium salt was made by precipitating with a solution of potassium carbonate. The calcium carbonate was filtered off and the filtrate evaporated to dryness.

Advantage was taken of the experience gained in connection with the oxidation of cymenesulphonic acid, it having been found that the conversion of cymenesulphonic acid into the substituted terephthalic acid is best effected in two stages. Paraxylenesulphonic acid in the form of the potassium salt was treated with chromic acid, the amounts of substances used being: 30 grams salt, 80 grams potassium pyrochromate and 120 grams sulphuric acid diluted with three times its volume of water. The oxidation was complete after boiling for three hours and a half. The whole was diluted with water, treated with chalk to remove chromic oxide and the excess of sulphuric acid, and then evaporated to dryness. The sulphotoluic acid was obtained in the form of the potassium salt.

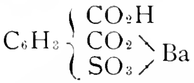
The potassium sulphotoluate was then further oxidized with potassium permanganate. The amount of salt used was that obtained by exactly neutralizing 17 grams of the acid potassium salt with the carbonate. To this quantity, dissolved in 600 cc. water, were added 100 cc. of a solution of potassium permanganate, prepared by dissolving 30 grams of salt in 200 cc. water. The reduction was completely effected by heating for half an hour on the water bath. Then 10 cc. of the permanganate solution were added, and the heating increased until this quantity was reduced, and so on. It was found that the total quantity of permanganate necessary to effect the oxidation was 24 grams, and the time occupied was about five hours. The precipitate of hydroxides of manganese was filtered off, the filtrate evaporated to a small volume and hydrochloric acid added. A crystallized salt separated which resembled the known acid potassium sulphoterephthalate in appearance. This was recrystallized a few times, but could not be obtained in pure condition. A small quantity of a salt richer in potassium than the sulphoterephthalate seemed to be present. Owing to the difficulty experienced in getting the potassium salt in pure condition, we concluded to convert it into the well-known barium salt. The potassium salt was dissolved in water and barium chloride added to the solution. A precipitate was formed which increased in quantity and became more crystalline in appearance on boiling. The precipitate thus formed conducted itself in every respect like the barium salt of sulphoterephthalic acid formed under like circumstances. The analyses of the salt gave the results here recorded.

I. 0.2448 gram salt lost 0.0112 gram H_2O at 290°, and gave 0.1048 gram $BaSO_4$.

II. 0.1856 gram salt gave 0.1072 gram $BaSO_4$.

III. 0.302 gram salt lost 0.0138 gram H_2O, and gave 0.1745 gram $BaSO_4$.

		Calculated.		Found.		
				I.	II.	III.
$C_8H_4O_7S$	...	244	61.15	...	...	...
Ba	...	137	34.34	33.82	33.95	33.97
H_2O	...	18	4.51	4.57	...	4.56
		399	100.00			

These results agree, as will be seen, with those required by a substance of the formula, 

$C_6H_3\left\{\begin{array}{l}CO_2H \\ CO_2 \\ SO_3\end{array}\right.\!\!\begin{array}{l} \\ \searrow \\ \nearrow\end{array}\!\!Ba$

$+ H_2O$, which is that of the *primary barium salt of sulphoterephthalic acid.*

In a recent communication* Jacobsen and Lönnies describe an acid obtained by them by oxidizing sodium α-metaxylenesulphonate with an excess of potassium permanganate. A careful study of this product, which the authors call α-sulphoisophthalic acid, will undoubtedly show that it is identical with the sulphoisophthalic acid first described by Remsen and Iles,† and obtained by them as a result of the oxidation of sulphaminemetatoluic acid. Mr. R. D. Coale is engaged in this laboratory in making a thorough comparison of the derivatives of sulphamineisophthalic and sulphoisophthalic acids. It has already been found that the salts of the two acids differ very markedly, and many of them crystallize well. As a necessary part of the investigation, sulphoisophthalic acid will be made by the oxidation of metaxylenesulphonic acid. From the

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* Berichte d. deutsch. chem. Gesell. 13, 1556.

† This Journal, 1, 121.

statements thus far made by Jacobsen, it is impossible to say positively whether he has ever really had the derivatives of sulphamineisophthalic acid in his possession or not. If the statement made by him* is correct, that the salt called by him potassium sulphamineisophthalate gives no evidence of the presence of nitrogen when tested by Lassaigne's method, then it is absolutely certain that he did not have the sulphamine acid, for this gives the reaction for nitrogen without difficulty. On the other hand, we must not forget the remarkable fact that this body, in which the delicate test of Lassaigne can not detect the presence of nitrogen, gives up its nitrogen in the form of ammonia, and that the amount of nitrogen in the body which undoubtedly contains none has thus been determined by Jacobsen.† It being thus impossible to decide what substances Jacobsen has obtained, it will of course be impossible to use his results to aid in clearing up the character of the reactions which take place when sulphaminemetatoluic acid is oxidized under different conditions with potassium permanganate. This whole subject will be treated in a later paper, when it will be shown that everything that has been claimed in the earlier papers of this series is only confirmed by later work.

It seems desirable, however, in this connection to call special attention to this fact, that the reactions which have been described in connection with sulphaminemetatoluic acid, and which Jacobsen, by the aid of incomprehensible experiments, has attempted to show were erroneous, are repeated in connection with sulphamineparatoluic acid. It is proved, beyond the slightest doubt, that when *sulphamineparatoluic acid* is oxidized in neutral solution, it is converted into *sulphoterephthalic acid*, whereas, when the potassium salt is oxidized, or enough potassium hydroxide is added to neutralize the free acid, the product is the peculiar nitrogenous anhydride which has been called *terephthalic sulphinide.*

JANUARY, 1881.

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* Berichte d. deutsch. chem. Gesell. 12, 2317.

† Ibid. 11, 1532.

REVIEWS AND REPORTS.

Brief Review of the most important Changes in the Industrial Applications of Chemistry within the last few Years.

(Continued from p. 268.)

Materials and Processes connected with the Construction of Buildings.

Chief Building Materials for External Use: Stone and Brick.

Progress has been made in the manufacture of artificial stone, both as to the character of the material turned out and the scale upon which it is used. The first practically successful method of production was that of the original Ransome patent, but it involved heavy consumption of fuel in baking the blocks moulded from sand and solution of sodium silicate, with more or less defacement of the surface of the blocks by smoke. It has been generally replaced by the use of hardening solutions, chiefly that of calcium chloride, applied at ordinary temperature to the mass of silicious sand and soluble glass. One of the most interesting and valuable improvements is that by which the so-called "Victoria stone" is made. Blocks of concrete are moulded from hydraulic cement of good quality, and when dry these are immersed in a solution of sodium silicate, in which has been placed a quantity of silica in easily soluble form, usually of infusorial origin. This calcareous concrete is gradually hardened by the formation of calcium silicate, while the alkali liberated from the solution attacks and dissolves fresh portions of silica, a very limited quantity of soda thus becoming the carrier for a large amount of silica transferred to the hardening block. The process is economical, and diminishes the tendency to unsightly efflorescence of alkaline salts on the surface of the stone when used. The principle of forming by precipitation from successively applied solutions an insoluble silicate or aluminate with which to close the pores of natural stone, and so reduce the effect of weathering, has of late years been employed with moderate success in preserving the walls of public buildings; but, although the principle itself is sound, the difficulty of really penetrating the stone to any considerable depth with the solutions has tended to limit materially the practical value of the process. The manufacture of enormous blocks of concrete, sometimes of 250 or 300 tons in weight, to be lifted bodily from the place of their production and by means of floating derricks lowered to their positions in the foundation of sub-aqueous works, is a comparatively novel application of artificial stone, but involves questions of engineering management only, there being nothing new in the chemical aspect of the production of the blocks themselves. To a small extent iron furnace slag, cast into rectangular blocks as it flows from the furnace, has been brought into use as a building material instead of stone.

Probably the most notable change in the practice of brick-making has consisted in the widespread substitution of dry moulding under heavy pressure for the ancient method of moulding the clay with water enough to form a soft dough. The great saving of time arising from the bricks as moulded being at once ready for the kiln, coupled with the saving of space required for drying, reduction of labor in handling the bricks upon the drying yard, and avoidance of the risk of injury by rain on open yards or expense of sheds to guard against this, constitute very material advantages in favor of the more modern practice. Iron furnace slag, whose use in the form of cast blocks has been noted above, has also been sparingly applied, after crushing, to the manufacture of bricks. Great advances have been made in the production of ornamental tiles and the superior kinds of terra cotta for architectural use, but the improvement has been chiefly on the artistic side of the manufacture in form and coloring rather than in the purely technological direction. Although not strictly belonging to this division of the subject, it may be noted that in fire-proof brick for furnace linings and the like applications, improvement has resulted from the substitution for mixed materials as found in nature, often uncertain and variable in composition, of nearly pure silica (crushed quartz), of alumina in the form of beauxite, and of lime and magnesia in the Thomas and Gilchrist linings for Bessemer converters; these materials being in each case mixed with so much only of foreign matter of opposite chemical character (basic and acid respectively) as shall ensure compactness without fusion in burning.

Lime-burning, Mortar and Hydraulic Cements.

One of the chief modifications of practice in burning lime has been the invention of General Scott, R. E., for producing what is known as "selenitic lime," containing about 5 per cent. of uniformly distributed calcium sulphate, by introducing gaseous sulphur dioxide into the kiln during the burning. Quick and hard setting of the mortar made with this lime, and the possibility of using much more than the usual amount of sand, are the advantages which are reported as attained. It has been ascertained by later experiments that the same results can be obtained by simply adding gypsum to the water used in slaking ordinary lime at the rate of 2 to 5 per cent. on the weight of lime treated. The older Roman cement, made from natural hydraulic limestone, has been to a large extent displaced by the improved and greatly extended manufacture of "Portland cement," the latter obtained by intimately mixing in carefully regulated proportion, chalk or other calcareous material on the one hand, with clay or other silicious and aluminous matter on the other, carefully calcining and grinding the mixture. Instead of using water enough in mixing the materials to produce a fluid mud or slip, from which a large part of the water was removed by a tedious process of settling, careful grinding with but little water has been brought into use, and the waste heat from the calcining kilns is utilized in drying off the solid mud so obtained, each charge as dried being transferred to the kiln, and during its calcination furnishing heat for drying the next portion. The great extension of demand for hydraulic cement of late years has led to the suggestion of several new materials for this use, amongst which one of those attracting for a while much attention was Sorel's oxychloride of magnesium,* prepared by means of the "bittern" of sea-water, or the mother liquors from the treatment of Stassfurt carnallite, but none of these materials have to any large extent passed into general use. Recently a cement has been introduced by Ransome, made by burning a mixture of lime and pulverized blast-furnace slag, which has been reported upon in terms of high praise. It is said to set much more rapidly than Portland cement, to attain greater absolute hardness, and to be manufactured at less cost.

Stucco.

There have been various small changes announced in the methods of hardening gypsum for casts, mouldings, plastering walls, etc. Alum, as employed in Keene's cement, and borax, as used in making the so-called Parian cement, are probably still the chief materials for producing the hardening effect, which is applied not only to the original white gypsum but also to that with which pigments have been mixed in order to imitate the appearance of marble.

Few inventions in connection with the comfort of our dwellings would have more value than the production of a really satisfactory substitute for plaster on the inner surface of the walls. Such a material should combine lightness, smoothness of surface, moderate porosity, freedom from the brittleness which makes plaster so easily injured, adaptation to the production of decorative effect, capability of being washed, low conducting power for heat, incombustibility—or at any rate considerable power of resisting the progress of fire—and reasonable cheapness. Some of these properties are possessed by the sheets of "muralis" introduced a year or two ago for the purpose in question, which is made by rolling a mixture of linseed oil and ground vegetable fibre on to a strong cotton fabric, but in other respects this invention has not fulfilled the demands of proper wall covering and decoration. The problem is doubtless largely a mechanical one, but involves chemical considerations also.

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* Proposed also as a substitute for gypsum in making casts, etc., and as the cementing material in the production of artificial stone.

Preservation of Timber.

For this purpose numerous materials continue from time to time to be proposed. Of late years less extensive use has been made of saline preservatives than of the crude phenols from coal tar, coupled with the external use of coal tar or pitch varnish. Hatzfeld has introduced the use of tan liquor, followed by crude acetate of iron. Experiments by means of hydrostatic pressure, and those of Boucherie, involving the natural capillary action of the sap-bearing vessels of the timber, have led to further progress in the mode of mechanically introducing the preservative fluids of whatever kind into the interior of the wood to be treated. In the light of modern knowledge of the lower forms of life, much value would probably attach to a careful investigation of the direct effect of various supposed poisons upon dry rot, and other moulds and organisms whether belonging to the vegetable or animal kingdom, (including teredo, termite, etc.), which lead to the decay of timber. Hitherto the selection of materials used has been made pretty much on empirical grounds.

Glue and other Cements of various application.

In glue-making it has been shown that needlessly protracted boiling and the use of a high temperature produced by high-pressure steam greatly injure the quality of the product as to strength and adhesiveness. The practice has therefore been introduced with advantage of boiling under pressure equal or superior to that of the atmosphere only until soluble gelatine has been produced, and then boiling down in a vacuum pan until the proper consistence has been reached for solidification in the moulds. It is asserted that bleaching of the scraps of skin, etc., by means of a saturated solution of sulphurous acid before the boiling, not only yields glue of much lighter color and greater clearness and lustre, but also produces a swelling up of the material, probably analogous to that which occurs in the "raising" of hide to be tanned, which materially shortens the time required for boiling into glue. It has also of late been proposed to remove fat from the animal matter by preliminary exhaustion with petroleum spirit in order to facilitate the action of the water in the boiling process.

Among the many minor cements which have been brought into use of late years, a few of those most likely to prove permanently valuable, at least for special purposes, are the following. "Chromated glue," prepared by adding to solution of ordinary gelatine or carpenter's glue chromic acid or potassium pyrochromate, at the rate of about one-fifth the weight of the dry gelatine, this material becoming permanently insoluble in water after it has been used as a cement and exposed to light. Caseine, from curdled milk, dissolved with the aid of borax. Glycerine and well-dried litharge, producing a cement which sets even under water, and is said to resist some of the solvents most difficult to manage, such as benzene and carbon disulphide; the proportions recommended are 50 grams of litharge and 6 cub. centimetres of a mixture of 5 parts by volume of glycerine and 2 of water. Boettger's cement, made with fine precipitated chalk, stirred into solution of sodium silicate at 33° B, to which pigments may be added if desired, the mixture hardening in six or eight hours. The so-called "Spence's metal," a fused mixture of iron pyrites or other metallic sulphides with excess of free sulphur; this material, with a melting point reported as low as 160° C, while presenting a considerable amount of cohesive strength and power of resisting exposure to air and water, with low price, seems worthy of some attention, especially for making the joints of water pipes, etc., although the claims put forward in its behalf on its first announcement were rather extravagant. Although now far from new, the extremely valuable "Marine glue," of Jeffrey, does not seem to be as well known in this country as it deserves. Prepared by dissolving 1 part of india-rubber in crude benzene, and mixing with 2 parts of shellac by the aid of heat, the water-proof character of this cement, in connection with its slight elastic flexibility, the ease with which it is applied when warm, and the promptness with which it sets on cooling, make it a most useful substance in many applications to house construction and furniture, as well as on board ship, where it was originally intended to be chiefly employed.

Pigments for House-Painters' use.

In regard to the most important of these, white lead, there have been several variations of the long used processes of manufacture. Probably the most notable of these is the modern German process, carried out in masonry chambers of considerable dimensions, instead of the small earthen pots of the ancient Dutch method, steam, vapor of acetic acid, air and carbon dioxide being introduced in regulated amounts to act upon thin plates of cast lead. In connection with the processes in which, with a view to extension of surface, lead is used in pulverulent form instead of in plates, may be mentioned the method of pulverizing the metal, patented by Tuttle & McCreary in this country, by means of a jet of high pressure steam driven through a falling stream of molten lead. When pulverulent lead is used for the after manufacture there is always some risk of particles of metal escaping complete corrosion, and, on being ground up, injuring the whiteness of the resulting paint. Pattinson's white oxychloride of lead is, or was very recently, still manufactured, but does not play a very important part in the general supply. Zinc white has grown into much more extensive use than formerly, and the production of the oxide represents a valuable industry. Within the last few years a white oxysulphide of zinc, approximating in composition to $5ZnS.ZnO$, has been brought forward, made by precipitating sulphate or chloride of zinc solution with a soluble sulphide, roasting the product slightly at a cherry red heat, raking out from the furnace into water, grinding finely, and drying. Its beauty of appearance and covering power are very highly spoken of. Mixtures of zinc sulphide with barium sulphate, of generally similar character, have also been placed in the market. The production of lamp-black of great purity and beauty, from the smothered combustion of the natural hydrocarbon gas of the petroleum region, is a comparatively new industry ; this material is, however, too dear for general house-painters' purposes, and is more used for choice printing ink than as a pigment. Among the red colors, lead oxychromate has come to be manufactured pretty largely, as a spurious substitute for and an adulterant of vermilion, and under various trade names as an independent pigment. Red, violet and blue lakes, made with aniline colors, have come into use to some extent. Among blue pigments, the greatest extension of manufacture has occurred with ultramarine, not only as regards the very large quantity now annually turned out, but also the variety of tints obtained, reaching from blue to distinct violet and a tolerable red, as well as the long known green. A paper of last year by Heinze* illustrates the wide variation as to amount of product and cost from the different mixtures of materials in use amongst ultramarine manufacturers.

Of green colors, Guignet's green (chromic oxide) has come to be made more largely and of much greater brilliancy than formerly, but must still be counted among the dearer pigments. Barium manganate has been introduced as a green pigment, and is said to exhibit much greater permanence than might have been expected from its composition.

Vehicles for Paints.

In careful hands the boiling of linseed oil is improved by keeping the temperature down to the lowest necessary point, using steam heat instead of an open fire, though much of the boiled oil of commerce shows the effect of over-heating and needless darkening in color. Manganese borate and other substances have come into use as " dryers," but no very notable improvement in this direction has been announced. Mixed distemper colors have been rendered capable of preservation for some time before use by addition of carbolic acid in small quantity to the animal size. Soluble glass solution has been used to some extent in the production of a kind of emulsion as a vehicle for paints for outdoor use.

Varnishes.

Probably the most noteworthy change in the manufacture of varnishes has been the extension of use of dammar and kauri resin, in the treatment of which, however, much remains to be done in order to secure a thoroughly satisfactory product. The large amount of kauri resin obtainable in New Zealand, and its mode-

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* Polytechn. Journ. 231 ; 366.

rate price, render it well worth more careful examination as to its solvents and the conditions under which they should be used. It is said that more information on this subject has already been obtained by certain manufacturers than has been published.

The method of Violette for rendering copal, kauri, etc., more readily soluble by preliminary fusion *in closed vessels* at well-regulated temperature is apparently of real value.

APPENDIX TO BUILDING APPLIANCES.

A.—*Explosive Agents* (*used in blasting and otherwise*).

In the economy of gunpowder manufacture the most valuable improvement known to the writer is that introduced at the Confederate powder mills at Augusta, Georgia, by Col. G. W. Rains, in 1862 or '63, namely, incorporation of the materials by a process of steaming. The sulphur and charcoal were severally pulverized and bolted, the nitre, pulverized by disturbed crystallization, added to these, and the mass, roughly mixed, was moistened with water and introduced into horizontal cylinders of sheet copper 30 inches long by 18 inches in diameter. These cylinders revolved slowly on a common axis consisting of a heavy brass tube 3 inches in diameter, perforated within the cylinders by a number of holes ⅛ inch diameter. High-pressure steam was introduced through this tube, raising the temperature to the boiling point, while the water produced by condensation, added to that originally used to moisten the materials, reduced them to a semi-liquid slush, which was run out of the cylinders after about eight minutes' rotation. On cooling, this mud became a damp solid cake, the nitre, which in the state of boiling hot saturated solution had entered the minutest pores of the charcoal, now recrystallizing. The cake so produced was transferred to the incorporating mills, and under 5-ton rollers was in an hour brought to the condition of finished mill cake, ready to be cooled and granulated, while without the steaming process four hours' incorporation in the mills had previously been necessary to produce powder of the same first-class character. The capacity for work of the mills was thus practically quadrupled, the thorough saturation of the charcoal with nitre being accomplished by the steaming, while it remained for the rollers merely to complete the mixture of the whole mass and to give the required density to the mill-cake. The enormous increase in the size of ordnance has led to much greater pains being taken in regulating the density of the press-cake made from the crushed mill-cake by hydraulic pressure, and much attention has been given to producing grains, pellets and prisms of finished powder of determinate size and shape. As regards the proportions in which the materials of gunpowder are used, the researches of Noble and Abel have shown that much less difference in the work done on explosion is caused by very considerable variation of composition than would have been previously supposed likely, the production of a higher temperature on explosion being attended with the formation of a less volume (at normal temperature and pressure) of permanent gases, and *vice versá.*

The investigations of Lenk and Abel have determined the proper conditions for the manufacture, storage and use of gun-cotton, have rendered it a practically manageable explosive, especially in the form of compressed pulp, and one of special value in certain cases. The latest modification proposed in the process of making it is that of Aimé Girard,* who moistens the vegetable fibre to be treated with a very weak solution of sulphuric or hydrochloric acid, heats to 50° or 80° C, or allows the moistened material to stand at common temperature for some weeks, or instead of the liquid acid uses a current of moist gaseous hydrochloric acid, finally washing out thoroughly with water. The "hydro-cellulose" thus formed is acted upon with concentrated nitric acid in the usual way, and a product is obtained which is extremely friable, and which after reduction to impalpable powder is said to resemble dynamite in its simple fusion on contact with flame (?) and in the extreme violence of its explosion by a shock.

In making nitro-glycerol it has been found that the inconvenience and danger resulting from rise of temperature in the mixture may be obviated by first treating the glycerol at 30° C with three times its weight of concentrated sulphuric acid, forming sulphoglyceric acid, cooling, and adding to separately mixed and cooled nitric and sulphuric acid. The reaction is attended with little heating, is not complete until twenty-four hours or so after mixture, and produces a distinct layer of nitroglycerol, to be syphoned off and washed. While dynamite is still largely used, consisting of nitroglycerol given solid form by mixture with inert mineral matter, there have been numerous more or less successful attempts to produce energetic explosives by substituting for such mineral matter (infusorial silica) a solid substance or substances capable of contributing to the production of useful effect. The most interesting of these until recently was the "glyoxaline" of Abel, consisting of ordinary gun-cotton soaked with nitroglycerol, both substances being energetic explosives, and the latter supplying the surplus oxygen which the former needs to render complete combustion possible. To this mixture a still more convenient form has recently been given, the so-called "explosive gelatine" of Nobel, prepared by dissolving about 7 per cent. of photographer's pyroxyline (soluble gun-cotton) in nitroglycerol to a jelly, with which may advantageously be mixed 10 per cent. of the most highly explosive tri-nitro-cellulose. This new material is free from the disadvantage of the nitroglycerol separating, as from dynamite. For some purposes it is modified by the addition of a little camphor.

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* Comptes rendus, 88, 1322, and 89, 170.

Although of subordinate importance, the picrates should be mentioned as comparatively recent additions to the list of standard explosives.

Our general knowledge in regard to the phenomena of explosion has received important additions from the long-continued researches of Abel, Noble, Champion and Pellet, the information obtained having already led to valuable applications in practice, and serving to point out clearly lines for future investigation. Amongst the chief subjects already examined are: the distinction between detonative explosion, developed by sudden mechanical shock (as from a separate initiative explosion), and inflammatory explosion, brought about by the application of a burning body to some part of the explosive material; the effect of complete enclosure within strong walls, or simple surrounding of the explosive with air or other readily mobile material; the conditions of transmission of detonative explosion from one mass to another of the same explosive agent, or from an explosive of one kind to one of different nature; the influence of the physical state and mechanical condition of the explosive; the phenomena of explosion in a mass saturated with or surrounded by water; and the chemical character of the products, the temperature, and the gaseous tension developed under different circumstances of explosion.

B.—*Disinfectants.*

The increased attention bestowed of late years upon sanitary matters has led to the manufacture, on quite a large scale, of numerous materials claiming to be valuable as disinfectants. The real value of these, when genuine, it is not easy accurately to estimate in the present imperfect condition of our knowledge as to the nature of the evils to be combatted and the manner in which they should be attacked. Unfortunately, in too many cases there has been extensive adulteration of substances which in their proper condition might fairly be accepted with some confidence, and in too many cases also there has been ignorance displayed in the use as well as in the choice of materials for this purpose. As a single illustration of the need existing for much fuller investigation of the subject of disinfecting materials and methods, the recent observations of Dianin* may be referred to. It has been generally held that carbolic acid and chloride of lime, separately useful as disinfectants, should be viewed as "incompatibles," the former liable to be destroyed by the latter, with loss of activity on the part of both. Dianin finds that if these two materials be mixed, trichlor-phenol is at once produced with but little of the di- and mono-chlor-derivatives, and that the mixture, representing essentially the calcium compound of tri-chlor-phenol, possesses notably greater antiseptic activity than either of the original substances taken by itself. Among the many individual points calling for

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*Chem. Central-Blatt., 3 Nov. 1880, 689; quoting from a Russian journal.

accurate and unbiased scientific investigation, may be instanced the effects producible upon the lower forms of living organisms by very low temperatures, although this is a question for the physicist and biologist instead of the chemist. The extension given to our command of low temperatures by the various forms of the modern ice-machine has increased the tendency to rely upon refrigeration as a disinfecting process, while experiments made upon the vitality of seeds of the higher orders of plants, after exposure to extraordinary cold, have not, so far as parallel inferences may be drawn from them, been by any means encouraging as to the destruction of the living organisms of simple structure whose important relation to the propagation of disease we have so much reason for believing to exist.

Among the chief steps of progress in recent years in regard to the industrial production of disinfecting materials, may be noted the great increase in the manufacture of phenol and cresol from coal tar (as also their sodium and calcium compounds), and their production in a state of far greater purity than formerly, the introduction upon a smaller, but still a commercial scale, of thymol and other of the higher phenols (the value of the special claims made in favor of which may still be considered open to discussion), the preparation in a very large way of salicylic acid by Kolbe's synthetic process, the manufacture of oxidized products from turpentine through which air is passed in the presence of water, the comparatively cheap production of the permanganates by the economical arrangements of Tessié du Motay and others, the use of bromine vapor, the manufacture of certain saline substances, such as aluminum chloride and bromide, in large quantity and at low price, with special advantages as to some details of their application, but of moderate or doubtful activity, and the supply of some new porous absorbents, such as Stanford's sea-weed charcoal, usefully available for some purposes of disinfection, within such distances from the seat of their production as are not too great to allow of moderate charges for transportation.

J. W. MALLET.

(*To be continued.*)

RECENT PROGRESS IN AGRICULTURAL SCIENCE.

(Continued from p. 342.)

Metastasis.—By the term *Metastasis*, equivalent to the German "Stoffwechsel," we designate in general all those chemical changes in the constituents of the plant which are not accompanied by a production of organic matter. The metastasis of plants and of animals is very similar in its general character, while the "assimilation" of chlorophyl-bearing plants, that is, the production of new organic matter, is peculiar to them, and radically distinct from the processes in the animal body to which the same name is applied.

Proteid Metastasis.—Our increased knowledge of the constitution of the albuminoids, due to the labors of Hlasiwetz and Habermann, Schützenberger and Kühne,* has not been without fruit in the domain of vegetable bio-chemistry, and has aided in forming some very probable conclusions regarding the chemical changes involved in the respiration of plants, and in the transfer of albuminoids from seed to sprout and from one part of the plant to another.

The first step in this direction was made by Pfeffer in his investigations into the functions of asparagine in the plant.† This substance, which is one of the products of the artificial decomposition of albuminoids by acids or by the digestive juices, is also found abundantly in seedlings of many plants, particularly leguminous plants. According to Pfeffer's investigations, asparagine, being soluble in water and diffusible, passes from the seed into the young plant and is there reconverted into albuminoids, and in this way the comparatively insoluble nitrogenous matters of the seed are transferred to the young plant where they are needed. Pfeffer experimented on germinating seeds of leguminous plants, and showed that, while the albuminoids were transferred to the young plant in the way just described, they appeared also to pass unchanged from seed to sprout.

It was also observed that the occurrence of asparagine in the seedlings corresponded exactly with that of glucose. Both were formed together in the radicle, the caulicle, the petioles of the cotyledons, and finally in the latter themselves; both were found in the parenchyma, but not in the vascular bundles, of the stem, and disappeared together before reaching the vegetation point.

These facts led to the conclusion that the presence of carbohydrates or other non-nitrogenous matters is necessary to the reconversion of asparagine into albuminoids, and the truth of this conclusion was established by later experiments. In these experiments‡ seedlings of *Lupinus luteus*, a plant which produces large quantities of asparagine, were grown in an atmosphere kept free from carbonic acid, and were thus limited to the small amount of non-nitrogenous matters furnished by the seed. Under these circumstances the plants grew until the reserve matters of the seed were exhausted, and at this time were found to contain large quantities of asparagine—much more than plants of the same age grown in presence of carbonic acid, and apparently about the same amount as plants grown in the dark. No glucose could be detected, and starch was found only in the guard-cells of the stomata.

At the time of Pfeffer's investigations asparagine was almost the only amide body whose presence in plants had been detected. Since that time, however, numerous other bodies of the same class

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* See this Journal, 2, 204.

† Jahrb. wiss. Botanik, 8, 530.

‡ Botanische Zeitung, 1874, 240.

have been discovered, among which may be especially mentioned two, which seem always to result from the decomposition of albuminoids, viz., leucine and tyrosine. These and other amides were found to be formed in varying quantities and proportions during the germination of many seeds, and to be contained in beets and potatoes, where they served as a reserve of nitrogenous food and were reconverted into albuminoids in the second year's growth.

These results led to a modification of Pfeffer's theory, inasmuch as they showed that asparagine was not the only nitrogenous product of the splitting up of albuminoids in the seed, but the main features of that theory remained unchanged.

Borodin* appears to have been the first to show conclusively that the occurrence of asparagine is not confined to seedlings and to roots and tubers. He found by micro-chemical investigations that asparagine was present in the leaf-buds of many trees and shrubs, and that in cases in which it was not normally present it could be developed by cutting off the twig bearing the buds and cultivating it in water, *i. e.* by depriving it of its supply of non-nitrogenous materials from the body of the plant. The occurrence of asparagine is not confined, however, to the leaf-buds. Borodin found that asparagine accumulated in the most various parts of the plant (stem, leaf-stalk, leaves, leaflets, flowers, etc.), when they were separated from the plant and cultivated in water. He also observed in many cases the occurrence of another body, which was most probably tyrosine, and of a third, undetermined body.

These results differ from Pfeffer's in one very important respect. They show that amides are formed not only when reserve stores of albuminoids are to be transferred to growing parts of the plant, but also in parts of the plant where, so far as we know, the only form of albuminoids present is the albumin of the living protoplasm. To account for this fact, Borodin supposes that in connection with the growth, or more probably with the respiration of the plant, a continual decomposition and regeneration of the albuminoids of the protoplasm takes place. The albuminoids, he believes, split up, yielding asparagine and other amides, and a non-nitrogenous residue, which combines with the oxygen of the air, forming carbonic acid and water. The amides formed in this process, together with the non-nitrogenous matters formed by assimilation or brought by diffusion from other parts of the plant, form the material for the regeneration of albuminoids, while, by virtue of their solubility and diffusibility, they readily serve to nourish protoplasm at a distance from the spot where they are formed.

On this theory the respiration of the plant, while it takes place at the expense of its non-nitrogenous ingredients, requires, as the first stage of the process, that their atoms become part of the molecules of the protoplasmic albuminoids. This assumption has much in its favor, and is accepted as probable by most authorities.

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* Botanische Zeitung, 1878, 802.

Other observers have obtained results confirming those of Borodin. Kellner[*] found that numerous green fodder plants contain large quantities of non-albuminoid compounds, among which amides predominate, and also that these compounds are most abundant in young plants, while in those in which growth has nearly ceased they are largely converted into albuminoids.

Emerling[†] has investigated the distribution of amides in the bean plant (*Vicia faba maj.*), and has found, as the general result, that "those parts of plants which are actively growing and increasing their mass are richer in amides than older and more developed parts."

All these results are plainly in harmony with Borodin's theory, since they find the larger proportion of amides in those parts of plants where respiration and growth are most active, and where, according to that theory, they are most abundantly formed. It is true that it is in these parts of plants also that the amides are most actively regenerated to albuminoids; but in the first place it is a commonly observed fact that substances which serve as material for the formation of new tissue accumulate to a certain extent near the place where they are used, and in the second place, as we shall soon see, a modification of the theory which has been proposed by E. Schulze explains very simply the accumulation of amides in the growing parts of plants. Before passing to this, however, a few results obtained by Schulze[‡] in experiments with twigs of birch and horse-chestnut cultivated in water, may be mentioned. In the leaves of both was found asparagine, and also indications of the presence of other amides. Indeed, a substance was separated from the twigs of the horse-chestnut which gave the reactions of leucine.

As just stated, Schulze has proposed certain modifications of Borodin's theory. In Schulze's first paper on the subject,[§] which was published at about the same time as Borodin's paper, and independently of the latter, he propounded essentially the same views, but with considerable reserve. In his second article[||] he advances his theory with more positiveness and in greater detail. It is based on the facts already mentioned in this article, together with others, observed by himself and his co-laborers, regarding the proportions of the various amides found in plants and on their distribution in the plant.

He shows in the first place that while the decomposition of albuminoids in the plant yields, as already pointed out, essentially the same nitrogenous products as are produced by heating the albuminoids with acids and alkalies, the proportions in which the various amides are found in plants differ widely from those in which they are produced by the artificial decomposition of albuminoids.

For example, Schulze and Barbieri, in experiments on squash

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[*] Landw. Jahrbücher, 8, 1 Supp. 243.

[†] Landw. Versuchs-Stationen, 24, 113.

[‡] Landw. Jahrbücher, 9, 713.

[§] Ibid. 7, 411.

Ibid. 9, 689

seeds, determined as accurately as possible the quantities of the several amides produced in germination, and also in the artificial decomposition of the albuminoid of these seeds by hydrochloric acid and stannic chloride after the method of Hlasiwetz and Habermann. The results, from the nature of the case, are only approximate, but the observed differences are too great to be accidental. They were as follows:

	Germination (Per cent. of dry matter of seedlings.)	Artificial decomposition. (Per cent. of protein used.)
Glutamic acid	1·75	3·4
Aspargic acid	0.06	2.5
Tyrosine	0.25	2.0
Leucine	trace	20.0

The proportions in which the various amides were found in the two cases are strikingly different.

So, too, in the germination of the legumes, large quantities of asparagine are observed with but little leucine, while the albuminoids of these seeds when treated with acid yield much leucine and but little asparagine. Many other similar examples are not wanting.

In the second place, Schulze has made some interesting and instructive observations on the distribution of amides in the seedling, experimenting chiefly on lupines. According to Pfeffer the asparagine of these seedlings originates in the cotyledons by the decomposition of their albuminoids, and passes from them to other parts of the plantlet. Schulze, however, found that the cotyledons of germinating lupines contained *less* asparagine than the remaining parts of the seedlings, a fact which it is difficult to explain on the assumption that the asparagine originates in the cotyledons and passes from them by osmose to other regions of the seedling. At the same time he found that the other amide-like bodies which accompany asparagine in germinating lupines were most abundant in the cotyledons.

It is worthy of note, also, that Pfeffer found that asparagine appeared first in the radicle, and last of all in the cotyledons.

The recent investigations into the constitution of the albuminoids have rendered it very probable that they contain as constituent groups of atoms the several amides which are found to result from their decomposition, and that the differences between the various albuminoids are at least partly due to differences in the proportions of the several amide groups which they contain. If this view be the true one, it is, as Schulze remarks, difficult to imagine that the same albuminoid should, under some circumstances, yield, *e.g.*, much leucine and little asparagine, and under other conditions much asparagine and little leucine. Yet this is exactly what appears to be the case with the conglutin of lupines, as we have just seen.

To explain this seeming anomaly, Schulze supposes, in the first place, that *some of the amides are more easily reconverted into albuminoids than others.* Thus, in the case just mentioned, he supposes that the leucine resulting from the decomposition of the conglutin is a more available source of albuminoids to the plant than the asparagine, and that consequently the latter accumulates in the seedling. In the case of the squash, mentioned on p. —, it is the glutamine (or glutamic acid) which is least readily utilized in the plantlet, and which is consequently most abundant in it at any given time. In general those amides which are least easily reconverted into albuminoids are the ones which are most abundant.

This supposition alone, however, does not suffice to explain either the enormous accumulation of particular amides in certain cases or their peculiar distribution in the seedling already alluded to. For example, in lupine seedlings grown in the dark, as much as half of their total nitrogen has been observed to exist in the form of asparagine, while conglutin on treatment with acids or alkalies yields only about 2 per cent. of aspargic acid. Moreover, as we have seen, a larger proportion of this asparagine is found in the growing parts of the seedling than in the cotyledons where the decomposition of the conglutin must take place.

These facts lead most naturally to the further hypothesis that *an alternate formation and decomposition of albuminoids takes place* similar to the transitory starch building frequently noticed. This hypothesis permits us to consider the decomposition of albuminoids in the plant as analogous to, if not identical with, that occurring under the influence of acids and alkalies and of trypsin, and at the same time to explain the fact that the products of the decomposition are found in very different proportions in the two cases. Taking again the germination of the lupine as an illustration, our hypothesis supposes that the conglutin of the cotyledons first splits up into a mixture of leucine, tyrosine, asparagine, glutamine, etc. These amides are carried by diffusion to the growing parts of the plantlet, where they serve for the nutrition of the protoplasm of the cells and are reconverted into albuminoids. In this process those amides which are most easily reconverted are utilized first, while most of the asparagine seems to remain unacted on. The resulting albuminoids are supposed to be again decomposed into a mixture of amides which serve to nourish the protoplasm of remoter cells, while the asparagine is again left unassimilated. In this way, by repeated formations and decompositions of albuminoids, a considerable accumulation of asparagine might result *in the seedling*, while the cotyledons would naturally contain far less of it.

In later stages of growth the asparagine seems to be also assimilated and disappears, and in mature plants, where the vigor of assimilation is great, all the amides resulting from the decomposition of the protoplasmic albuminoids in respiration are rapidly reconverted into albuminoids, and can sometimes be detected only by cutting off the supply of non-nitrogenous materials, as in Borodin's experiments.

The theory which has been developed in the foregoing pages explains equally well the facts observed in seedlings and the results obtained by Borodin on mature plants, and presents them to us as different phases of the same phenomenon; it is in accordance with Borodin's conclusions concerning the respiration of plants; and finally it throws some light on Pfeffer's observation that the cells of the vascular bundles in the stems of germinating lupines and other legumes are rich in albuminoids, which, according to this theory, were formed from amides and serve in turn as the source for further production of amides.

To recapitulate briefly, the theory assumes that the production of amides in the plant (except from the reserve albuminoids of the seed, if such a production takes place) is a normal function of the living protoplasm and part of the process of respiration. The oxygen of the air unites with the non-nitrogenous residue of the protoplasm, producing carbonic acid and water, while the fate of the amides depends upon the supply of non-nitrogenous matters. If this is abundant, as in mature plants, a rapid regeneration of albuminoids takes place, and little or no residue of amides can be detected. When the supply of non-nitrogenous matters is less abundant, as in germination, or when it is artificially suppressed, only those amides which are most easily reconverted into albuminoids suffer this change, the others accumulating to an extent depending on the amount of non-nitrogenous matter supplied and on the opportunity for assimilation. In any case those amides which are utilized are combined with non-nitrogenous matter and become part of new protoplasm, situated perhaps at a distance from the source of the amides, ready to be again decomposed in the same way. Thus the respiration of the plant, while taking place at the expense of non-nitrogenous substances, is performed by the protoplasm, and incidentally, so to speak, produces soluble and diffusible nitrogenous compounds for the nourishment of other protoplasm.

The theory described in the above paragraphs regards the amides solely as products of the regressive changes of the albuminoids. In the case of plants which have passed beyond the stage of dependence on the reserve matters of the seed, another view is possible, viz., that they are intermediate products in the formation of albuminoids from inorganic nitrogen compounds. This view is a very plausible one, but is difficult of proof. It is certain that amides are formed from albuminoids in the plant, and are reconverted into them, and it is difficult, if not impossible, to say in any given case that the amides whose presence is observed cannot have had their origin in albuminoids and must have been derived from nitric acid or ammonia. Consequently, while bearing in mind the possibility of such a source for some of the amides, we cannot yet go beyond the acknowledgment of its possibility, while the functions of the amides in the translocation of albuminoids are, in their main features, well established.

H. P. ARMSBY.

NOTES.

Properties of Ozone.

HAUTEFEUILLE and CHAPPUIS are carrying on an investigation of ozone, more particularly of its physical properties, and have already reached results of interest. With a view to obtaining a mixture rich in ozone, they first study[*] the influence of pressure and temperature on the formation of ozone from oxygen by means of electrical discharge. Their results show that the tensions of transformation are not a function of temperature alone, but also of pressure; hence the equilibrium between oxygen and ozone can not be analogous to that which is established in the decompositions of fixed combinations, and in the production of saturated vapors from solids or liquids. Their figures show, however, that the ratio of the volume of ozone to the volume of the whole mixture is nearly independent of pressure within considerable limits, and hence that there is an analogy between the transformation of oxygen under electrical influence and the dissociation of gases; for in the case of hydriodic acid, and others, at certain temperatures, the dissociation is limited by tensions sensibly proportional to the total pressure. The proportion of hydrogen and iodine liberated increases as the pressure diminishes, so also the proportion of oxygen to ozone. The combination of hydrogen and iodine and the transformation of oxygen into ozone, both absorbing heat, should then be favored by an increase of density.

To obtain therefore a mixture rich in ozone,[†] they allowed oxygen to remain for one-quarter of an hour in the apparatus for alternating discharges, the latter being plunged in methyl chloride to produce a low temperature. The gas was then passed into the reservoir of Cailletet's condensing apparatus, previously exhausted and reduced to —23°. They were thus enabled in one and a quarter hours to fill the reservoir with a mixture containing a large proportion of ozone. This was then compressed by mercury at 0°, the reservoir being kept at —23°. The mercury was not acted upon by the gas as much as was anticipated, but the treating by compression gave greater difficulty. However, they succeeded in obtaining a high tension. At the first stroke of the piston the capillary tube showed an azure blue color which increased with increase of pressure. When the pressure reached several atmospheres the color of the gas was indigo blue, and that of the meniscus of mercury seen through the glass tube was steel-blue. The color disappeared when the tension

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[*] Comptes rendus, July 26th, p. 228.

[†] Ibid. Sept. 20th.

was lessened. Sudden expansion after a pressure of seventy-five atmospheres caused a thick fog, a certain sign of liquefaction or even solidification which is reached with oxygen only after a pressure of three hundred atmospheres.

A comparative study of mixtures of oxygen and ozone and oxygen and carbon dioxide showed that ozone is a little less easily liquified than carbon dioxide. The mixture of oxygen and ozone must be cooled when compressed, or heat is generated and a strong detonation follows accompanied by heat and yellow light. Berthelot has shown that the heat of formation of ozone is —14.8 cal. for $O_3 = 24$, and the experiments of Hautefeuille and Chappuis show that it is also explosive. This fact can be partly observed at ordinary temperature; for if the gas obtained from the electrical apparatus be passed into a capillary tube placed in water at 25° and rapidly compressed, ozone is often destroyed with explosion. If the same is maintained at —23° and ten atmospheres of pressure, it can be kept for hours, if separated from the mercury by a layer of sulphuric acid. The azure blue color can be seen in this case almost as well as in the first, it being perceptible in a tube 1 mm. in diameter in the dimly lighted room of the Ecole Normale. The color is as characteristic of ozone as its odor, being visible at all tensions if the gas be in sufficiently thick layer. It can be seen by holding between the eye and some white surface a tube 1 meter long through which passes a current of oxygen from Berthelot's electrical apparatus.

The same investigators next study the effect of certain gases on the transformation of oxygen into ozone.* They find that the presence of a very small quantity of chlorine prevents the formation of ozone, or destroys it after it is formed. The presence of nitrogen increases the proportion of ozone formed at low pressure by nearly one-half. With hydrogen for the same temperature and tension of oxygen, the proportion of ozone is greater than with nitrogen. With fluoride of silicon the proportion reaches even .40; but in this case the form of discharge changes. In order to furnish comparable results the form of discharge as well as the temperature should remain the same.

They next endeavored to obtain ozone as a permanent liquid.† At two hundred atmospheres and —23° the gas was blue, but no liquid appeared. A part of the tube was then reduced to —88° and the color appeared three or four times as intense as at —23°. The mercury was frozen and unacted upon by the ozone, but there was no liquefaction. A large proportion of carbon dioxide was then added to the mixture. At —23° and with slow increase of pressure a liquid appeared colored blue, the same as the gas above it. This liquid was permanent while the pressure continued, being a solution of ozone in liquid carbon dioxide. Although unsuccessful so far in their attempts to obtain liquid ozone, they hope to succeed by

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* Comptes rendus, Nov. 8th, p. 762.

† Ibid. Nov. 15th.

compressing at low temperature a mixture of oxygen and ozone obtained at —88° and containing more than 50 per cent. of ozone.

The appearance of color enabled them to show the large proportion of ozone in the mixture obtained by submitting carbon dioxide to the electrical discharge, thus confirming the supposition that the high oxidizing power of this mixture observed by Berthelot is due to ozone rather than to a percarbonic acid.

As the blue color of ozone recalled that of the sky, Chappuis* undertook to compare the absorption spectrum of the former with the atmospheric absorption bands and found several coincidences, but at his last report had not completed the study.

A. V. E. Y.

On new Ethers of Carbonic Acid.

In the last number of this Journal attention was called to an investigation by Ludwig Schreiner which led to the remarkable conclusion that there are two isomeric substances of the formula $CO\begin{cases}OCH_3\\OC_2H_5\end{cases}$, and also two substituted ureas $CO\begin{cases}NH.C_2H_5\\NH.CH_3\end{cases}$. The results of Schreiner would of course necessitate the abandonment of the now commonly accepted view regarding the equivalence of the four affinities of carbon. Almost immediately after the publication of Schreiner's paper, there appeared another on the same subject by Röse, working in Geuther's laboratory. Strange to say, however, the results reached by Röse are exactly the opposite of those reached by Schreiner. Röse describes a number of new ethers of carbonic acid, including such as contain only one kind of residue, and such as contain two kinds. The methylethyl ether, whether prepared by first introducing methyl and then ethyl, or in the opposite way, was found to have exactly the same properties. The same is true of the methylpropyl, methylbutyl, ethylbutyl and ethylamyl ethers. The boiling points, specific gravities and refractive indices of the members of each pair of isomerides are found to be exactly the same. Further investigation will be necessary to decide which of the two investigators is in the right. As the matter is one of fundamental importance, it is desirable that it should be definitely cleared up as soon as possible.—(*Annalen der Chemie,* 205, 227.)

The Atomic Weight of Glucinum.

Nilson has replied to Lothar Meyer on the subject of the atomic weight of glucinum. Meyer attempted to show that the most natural conclusion to be drawn from the experiments of Nilson and Pettersson is that the atomic weight of this element is 9.1, as has hitherto been assumed. Nilson, however, calls attention to certain facts which Meyer apparently lost sight of, and which put quite a different light on the matter. The molecular heats of the oxide of glucinum and the sulphate are those which the theory requires on

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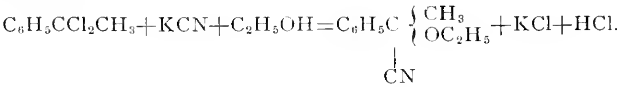
* Comptes rendus, Dec. 13th.

the supposition that the compounds have the formulas Be_2O_3 and $Be_2 3SO_4$. The values found correspond to those for the oxide and sulphate of aluminum. If the oxide of glucinum has the formula Be_2O_3, then the element has the atomic weight 13.65, or exactly half the atomic weight of aluminum.—(*Ber. d. deutsch. chem. Gesell.* 13, 2035.)

Synthesis of Tropic Acid.

Ladenburg and Rügheimer have achieved a brilliant success in their studies upon the alkaloids. They have previously shown that hydratropic, atrolactinic, atropic and tropic acids can be transformed one into the other. The synthesis of any one of the first three acids would hence lead to that of tropic acid itself. They have now succeeded in building up atropic acid. For this purpose they start with acetophenone, $C_6H_5.CO.CH_3$. This is converted into dichlorethylbenzene $C_6H_5CCl_2CH_3$ by treating with phosphorus pentachloride. The chloride is then warmed with an alcoholic solution of potassium cyanide, when the following reaction takes place:



$$C_6H_5CCl_2CH_3+KCN+C_2H_5OH=C_6H_5\underset{\displaystyle CN}{\underset{|}{C}}\left\{\begin{matrix}CH_3\\OC_2H_5\end{matrix}\right.+KCl+HCl.$$

Now, on boiling the product with baryta-water the cyanide is converted into the corresponding acid thus:

$$C_6H_5—C\left\{\begin{matrix}CH_3\\OC_2H_5\\CN\end{matrix}\right.+ba(OH)+H_2O=C_6H_5—C\left\{\begin{matrix}CH_3\\OC_2H_5+NH_3.\\COOba\end{matrix}\right.$$

The acid formed is ethylatrolactinic acid. When treated with hydrochloric acid it readily yields atropic acid, $C_6H_5—C\left\{\begin{matrix}=CH_2\\COOH\end{matrix}\right.$; and this acid may be converted into tropic acid by first adding hypochlorous acid and replacing by means of hydrogen the chlorine of the product, the reactions being:

$$C_6H_5—C\left\{\begin{matrix}CH_2\\COOH\end{matrix}\right.+HOCl=C_6H_5—CCl\left\{\begin{matrix}CH_2OH\\COOH\end{matrix}\right.$$

and $$C_6H_5—CCl\left\{\begin{matrix}CH_2OH\\COOH\end{matrix}\right.+H_2=C_6H_5—CH\left\{\begin{matrix}CH_2OH\\COOH\end{matrix}\right.+HCl.$$

Tropic acid.

—(*Ber. d. deutsch. chem. Gesell.* 13, 2041.)

On the Hydrocarbons of American Petroleum.

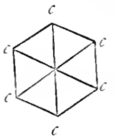
The results recently reached by Beilstein and Kurbatow in their examination of the petroleum from the Caucasus, a brief account of which was given in the last number of this Journal, have led the authors to examine American petroleum. By means of fractional distillation heptane was separated from petroleum. It boiled at 95-100° and had the specific gravity 0.7192. The analysis showed that the substance contained a slightly larger amount of carbon and smaller amount of hydrogen than the formula C_7H_{16} requires. This heptane was heated with four parts of ordinary nitric acid (sp. gr. 1.38) as long as nitrous fumes were given off. From the layer of oil floating on the acid at the end of the operation, heptane was again isolated. It was found to boil at 98.5-99.5°, and has the specific gravity 0.6967. The analyses now gave results in accordance with the formula C_7H_{16}. This perfectly pure heptane is not attacked materially by nitric acid.

It is thus shown that besides the hydrocarbons C_nH_{2n+2}, there are other hydrocarbons, containing less hydrogen, in American petroleum. Crude heptane had a higher specific gravity, contained less hydrogen than the formula C_7H_{16} requires, and was attacked by nitric acid.

It seemed probable that American petroleum might contain the same addition products of the benzene hydrocarbons as were found in Caucasian petroleum. On treating that portion of the American variety which boils between 115° and 120°, with a mixture of concentrated nitric and sulphuric acids, a small quantity of *trinitroisoxylene* was obtained. Hence it is seen that, besides the hydrocarbons C_nH_{2n+2}, American petroleum contains others of the general formula C_nH_{2n}.—(*Ber. d. deutsch. chem. Gesell.* 13, 2028.)

Concerning the Formula of Benzene.

In a recent paper on thermochemical investigations on hydrocarbons, Julius Thomsen drew the conclusion that the commonly accepted formula of Kekulé for benzene is incorrect, and that the formula is more probable. At the same time Brühl concludes from his investigations that Kekulé's formula is correct. Brühl bases his conclusion on the fact that the molecular refraction of benzene is that which, according to his rule, a substance with three double links would require. To this Thomsen now replies. He says: "The molecular refraction is considered as an expression of the density of the body, and the conclusion is hence drawn that, if the body has a higher molecular refraction than the normal, calculated from its elements, this indicates a greater density which is caused by a stronger linking of the carbon atoms of the body; and the conclusion is further drawn that this greater density of benzene can be explained by assuming three double linkages.



"The explanation of the greater density may be just as easily and consistently explained in another way. According to the theory, a linking of the six carbon atoms by six single links would give the normal density and the normal molecular refraction; each carbon atom would then be in combination with two others. But the six carbon atoms still have six affinities, which can give three single linkages. If these three affinities are employed to unite each carbon atom with three others, then, if the linkages have any influence on the density, a linking of *each* carbon atom to three other carbon atoms must necessarily cause a greater density than would be caused by union of each carbon atom with only two others.

"The supposed greater optical density, *i.e.*, the increased molecular refraction of benzene, may hence be explained just as easily by assuming the presence of nine single links, which unite each carbon atom with three others, as by assuming three double links." —(*Ber. d. deutsch. chem. Gesell.* 13, 2166.)

Arsinobenzoic Acid.

La Coste has oxidized tolylarsinic acid, $C_6H_4\left\{\begin{matrix}CH_3\\ AsO(OH)_2\end{matrix}\right.$, and obtained a substance which he calls benzarsinic acid, $C_6H_4\left\{\begin{matrix}COOH\\ AsO(OH)_2\end{matrix}\right.$. When benzarsinic acid is heated, it gives off water, and the anhydride is formed. This is *arsinobenzoic acid*, $C_6H_4\left\{\begin{matrix}COOH\\ AsO_2\end{matrix}\right.$, a compound analogous to nitrobenzoic acid, and differing from the latter only in the fact that it contains the element arsenic in the place of nitrogen.—(*Ber. d. deutsch. chem. Gesell.* 13, 2176.)

Baeyer's Method for the Synthesis of Indigo.

Baeyer describes two processes for the synthetic preparation of indigo, both of which start from cinnamic or phenylacrylic acid $C_6H_5.CH.CH.CO_2H$.

In both processes nitrogen is introduced into the molecule in the form of NO_2 in the phenyl. Only the ortho-nitro acid is capable of forming indigo. Orthonitrocinnamic acid being prepared, Baeyer transforms it into orthonitropropiolic acid or into orthonitrophenyloxyacrylic acid by processes identical with those which are employed for transforming cinnamic acid into phenylpropiolic acid or into phenyloxyacrylic acid. The two ortho-nitro acids are transformed into indigo by simple reactions. The different steps in the synthesis are these:

1. *Preparation of orthonitrophenylpropiolic acid.*—Orthonitrocinnamic acid is brominated; there is formed $C_6H_4(NO_2) . C_3H_3Br_2O_2$. Boiling alcoholic solutions of the alkalies extract 2HBr from this body; there remains $C_6H_4(NO_2)(C_3HO_2)$, orthonitrophenylpropiolic acid.

2. *Preparation of orthonitrophenyloxyacrylic acid.*—Orthonitrocinnamic acid is treated with chlorine, when orthonitrophenylchlorolactic acid is formed.

$$C_6H_4(NO_2)—CH=CH—COOH+HClO=$$
$$C_6H_4(NO_2)—CH(OH)—CHCl—COOH.$$

When this acid is treated with caustic alkalies in solution, it loses the elements of hydrochloric acid, and is transformed into orthonitrophenyloxyacrylic acid.

$$C_5H_4(NO_2)—CH(OH)—CHCl—COOH=HCl+C_6H_4(NO_2)—$$
$$C(OH)=CH—COOH.$$

3. *Preparation of indigo.*—The action of heat alone converts orthonitrophenyloxyacrylic acid into indigo.

$$C_9H_7NO_5=C_8H_5NO+CO_2+H_2O+O.$$

The reaction takes place at 110° C. The yield by this method is not good.

With orthonitrophenylpropiolic acid the process takes place more regularly. It requires the simultaneous action of an alkali and a reducing agent.

$$C_9H_5NO_4+H_2=C_8H_5NO+CO_2+H_2O.$$

Baeyer recommends the use of a mixture of glucose and an alkaline carbonate. The transformation takes places at 110° and the indigo separates in crystalline form. Baeyer much prefers the latter to the former method. It presents a peculiarity which deserves special notice: it is that the reaction can be brought about directly by the fabric.

The textile fiber is impregnated with a mixture composed of orthonitrophenylpropiolic acid, an alkaline substance and a solution of glucose, when it is exposed to the desired temperature, for example, in a current of superheated steam. The indigo blue will be produced in the material, and will be intimately fixed on the fiber.

If artificial indigo should be too expensive to replace the natural product in the processes of dyeing, it might still be that its formation directly on the fiber could be of advantage. Its use will depend less on its price than on the regularity of its formation.—(M. Rosenstiehl in *Annales de Chimie*, 21, 286; and *Ber. d. deutsch. chem. Gesell.* 13, 2254.) *

Dr. FERD. FISHER has undertaken the editing of the *Jahresbericht für die chemische Technologie*, succeeding Prof. von Wagner, who recently died. Dr. Fisher has for a long time past edited *Dingler's Polytechnisches Journal.*

Professor B. C. BRODIE, Bart., F. R. S., D. C. L., the eminent English chemist, died November 24, 1880. He was born in London in 1817. He studied under Liebig at Giessen, and undertook his first investigation there in 1845. From this time he was actively engaged in research. In 1855 he was appointed Professor of Chemistry in the University of Oxford. In 1866 he published his

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* The original paper of M. Rosenstiehl contains a number of serious errors. In the above abstract these have been corrected.—ED.

"Calculus of Chemical Operations," in which he puts forth novel views respecting the nature of chemical change.

Dr. William Heintz, Professor of Chemistry at the University of Halle, died recently at the age of sixty-three years.

Dr. John Stenhouse, F. R. S., the well-known English chemist, died December 31. He held at one time the lectureship in chemistry in St. Bartholomew's Hospital, London. In 1865 he succeeded Dr. Hofmann as non-resident assayer to the Royal Mint.

A Cincinnati Chemical Society has just been organized, with the following officers: President, F. W. Clarke; Vice President, F. Roeder; Secretaries, W. L. Dudley and Alfred Springer; Treasurer, H. F. Reum. Monthly meetings will be held, for the reading of papers, and discussion.

RECENT PUBLICATIONS RELATING TO CHEMISTRY.

I.—American.

Armsby, H. P. Manual of Cattle-Feeding: a Treatise on the Laws of Animal Nutrition and the Chemistry of Feeding-Stuffs in their Application to the Feeding of Farm Animals. New York: Wiley. $2.50.

Cooke, J. P. Religion and Chemistry: a Re-statement of an old Argument. Newly revised edition. New York: Scribner. $1.50.

Douglas, S. H., and Prescott, A. B. Qualitative Chemical Analysis. 3d edition revised. New York: Van Nostrand. $3.50.

Legg, J. W. Guide to the Examination of Urine. 5th edition. Reprint. Philadelphia: P. Blakiston. 75 cents.

Semple, C. E. A. Aids to Chemistry. Cloth, 50 cents; paper, 25 cents. Reprint. New York: Putnam.

Muter, J. Introduction to Pharmaceutical and Medical Chemistry. New edition. Reprint. Philadelphia: Blakiston. $6.00.

II.—English.

Armstrong, H. E. Introduction to the Study of Organic Chemistry. 2d edition. London: Longmans. 3s. 6d.

Brodie, B. C. Ideal Chemistry. London: Macmillan. 2s.

Miller, W. A. Elements of Chemistry, Theoretical and Practical. Part 3. Chemistry of Carbon Compounds, or Organic Chemistry. Section 1. 5th edition. London: Longmans. 31s. 6d.

Morris, D. A Class-book of Inorganic Chemistry. New edition. London: Philip. 2s. 6d.

ROSS, W. A. Alphabetical Manual of Blowpipe Analysis. London: Trübner. 5s.

ROSS, W. A. Pyrology, or Fire Chemistry. London: Trübner. 36s. New ed.

WILLS, T. The Life of Thomas Wills, Demonstrator of Chemistry, Royal Naval College, Greenwich. By his Mother, Mary Wills Phillips, and J. Luke. Nisbet. 3s. 6d.

WURTZ, A. The Atomic Theory. Translated by E. Cleminshaw. London: Paul. 5s.

III.—FRENCH.

CHAPINS, A. Role chimique des ferments figures. Baillière. 3fr. 50.

GORUP-BESANEZ. Traité de chimie physiologique. Traduit et annoté par F. Schlagdenhauffen. 2 vol. Dunod. 32fr.

LACOTE, A. Synthèse des corps azoté. Baillière. 2fr. 50.

MAUMENÉ, E. J. Théorie générale de l'action chimique. Dunod. 9fr.

PISANI, F. Traité pratique d'analyse chimique qualitative et quantitative. G. Baillière. 3fr. 50.

SCHÜTZENBERGER, P. Traité de chimie générale, comprenant les principales explications de la chimie aux sciences biologiques et aux arts industriels. Tome II. Hachette. 14fr.

WALLACH, O. Tableaux servant à l'analyse chimique. Traduit par J. Krutwig. Reinwald. 2fr. 50.

IV.—GERMAN.

ARENDT, R. Technik der Experimentalchemie. 1 Bd. 1, 2 Lief. Leipzig: Voss.

AUERBACH, G. Das Anthracen und seine Derivate. 2 vermehrte Aufl. Braunschweig. Vieweg u. Sohn. M. 7.20.

BEILSTEIN, F. Handbuch der organischen Chemie. 1 Lief. Leipzig: Voss. M. 3.

BELOHOUBEK, A. Ueber den Einfluss der geologischen Verhältnisse auf die chemische Beschaffenheit d. Quell- und Brunnenwassers. Prag: Rziwnatz. M. 1.20.

BERSCH, J. Die Essig-Fabrikation. 2 Aufl. Wien: Hartleben. M. 3.

BUNSEN, R. Flammenreactionen. Heidelberg: Koester. M. 1.

DUMREICHER, O. Untersuchungen über die Einwirkung von Zinnchlorür auf die Stickstoffsauerstoffverbindungen. Wien: Gerold's Sohn. M. 0.50.

ELSNER, F. Die Praxis d. Nahrungsmittel-Chemikers. Leipzig: Voss. M. 4.

FISCHER, F. Die chemische Technologie des Wassers. Braunschweig: Vieweg. M. 11.60.

FISCHER, F. Leitfaden der Chemie und Mineralogie Hannover: Hahn'sche Buchh. M. 2.80.

FALCK, F. A. Lehrbuch der praktischen Toxikologie. Stuttgart: Enke. M. 8.

GERBER. Chemisch-physikalische Analyse der verschiedenen Milcharten und Kindermehle. Bremen: Heinsius.

GODEFFROY, R. Compendium der Pharmacie. 1, 2 Lief. Wien.

GROSS, G. Die Stickstoffgruppe der neueren Chemie und die der Atomen ihrer Elemente zuzuschreibende Valenz. Hamburg: Jenischen. M. 1.

GROSSE-BOHLE, A. Ueber das optische Verhalten d. Senarmontits und der regulären arsenigen Säure. Lüdinghausen: Rademann. M. 2.

HANDBUCH der chemischen Technologie. Hrsg. v. P. Bolley, fortgesetzt v. R. Birnbaum. 5 Bd. Chemische Verarbeitung der Pflanzen- und Thierfasern. 4 Lfg. Die künstlich erzeugten organische Farbstoffe, von R. Meyer. Braunschweig: Vieweg. M. 10.

Hempel, W. Neue Methoden zur Analyse der Gase. Braunschweig: Vieweg. M. 5.

Hendess, H. Allgemeine Giftlehre. Berlin.

Heppe, G. Katechismus der Chemikalienkunde. Eine kurze Beschreibung der wichtigsten Chemikalien des Handels. Leipzig.

Herzig, J. Ueber Phenolorthosulfosäure und ihr Verhalten gegen schmelzende Kali. Wien: Gerold's Sohn. M. 0.20.

Jahresbericht über die Fortschritte der Chemie. Hrsg. von F. Fittica. Für 1879. 1 Heft. Giessen.

Jahresbericht über die Fortschritte auf dem Gebiete der reinen Chemie. Hrsg. von L. Medicus und W. Staedel. Für 1879. 1 Hälfte. Tübingen.

Jahresbericht über die Leistungen der chemischen Technologie mit besonderer Berücksichtigung der Gewerbestatistik für das Jahr 1879. Hrsg. von R. v. Wagner. XXV. Leipzig.

Kolbe, H. Ausführliches Lehr- und Handbuch der organischen Chemie. 2 Aufl. 1 Band. Braunschweig.

Liebermann, L. Grundzüge der Chemie d. Menschen, für Ärzte und Studierende. Stuttgart: Enke. M. 6.

Maercker, M. Die Kalisalze und ihre Anwendung in der Landwirthschaft. Berlin: Wiegand, Hempel und Parey. M. 3.

Meyer, Lothar. Die modernen Theorien der Chemie und ihre Bedeutung für die chemische Mechanik. 4 Aufl. 1 Buch, die Atome. Breslau: Marnschke und Berendt. M. 5.

Michaelis, A. Einführung in die allegemeine Chemie und die physikalisch-chemischen Operationen. Braunschweig: Vieweg. M. 6.

Mikosch, K., und A. Stöhr. Untersuchungen über den Einfluss d. Lichtes auf die Chlorophyllbildung bei intermittirender Beleuchtung. Wien: Gerold's Sohn. M. 0.25.

Muspratt's theoretische, praktische und analytische Chemie in Anwendung auf Künste und Gewerbe. Frei beiarb. von B. Kerl und F. Stohmann. 3 Aufl. 7 Bd. 4 Lfg. Braunschweig: Schwetschke und Sohn. M. 1.20.

Pauly, C. Einführung in die quantitative chemische Analyse. Braunschweig: Haffeiburg. M. 4.

Richter, V. v. Chemie der Kohlenstoffverbindungen, oder organische Chemie. 2 Aufl. Bonn.

Wagner, R. v. Handbuch der chemischen Technologie. 11 Aufl. Leipzig: Wiegand. M. 12.

Wallach, O. Tabellen zur chemischen Analyse. I. und II. Theil. Bonn.

Wiesemann, Th. Ursachen der Haupt-Naturerscheinungen, wie: Schwere, Härte, Elastizität, Licht, Farben, Wärme, Elektrizität, chemische Verbindungen, u. s. w. Aus einem einzigen Fundamentel-Princip, logisch-mathematisch entwickelt. Brüssel.

Zuelzer, W. Lehrbuch der Harn-Analyse. Berlin.

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DORPAT.

Keussler, E. v. Untersuchung der chrysophansäureartigen Substanz der Sennesblätter und der Frangulinsäure nebst Vergleichung derselben mit der Chrysophansäure des Rhabarbers.

Koroll, J. Quantitativ-chemische Untersuchungen über die Zusammensetzung der Kork- Last- Sclerenchym- und Markgewebe.

Pfeil, T. Chemische Beiträge zur Pomologie.

Poehl, A. Untersuchung der Blätter von Pilocarpus officinalis (Jaborandi) in pharmacognostischer und chemischer Beziehung.

Scheibe, E. Darstellung und Beschreibung Borcitronensäure und ihrer Salze.

Freiburg.

Barisch, F. Ueber einige Derivate der Bromzimmtsäure.

Brand, J. Ueber einige Salze und Abkömmlinge der Hydroxycaprylsäure.

Dannenbaum, H. Zur Kenntniss des Cinchonidins.

Glassner, R. Beiträge zur Kenntniss des Strychnins.

Halberstadt, W. Ueber Metanitroparanitrobenzoësäure, eine neue fünfte isomere Dinitrobenzoësäure, und das Verhalten der Paranitrobenzoësäure gegen substituirende Agentien.

Helpenstein, J. Ueber die Einwirkung von Ammoniak auf Bibrombernsteinsäure, und über Diamidobernsteinsäure.

Kemperdick, H. Beiträge zur Kenntniss des Cinchonidins.

Koerner, H. Ueber Storesin, einen Gemengtheil des flüssigen Storax, und einige Derivate derselben.

Krusemark, P. Die Zersetzungsproducte der Citra- und Mesabibrombrenzweinsäure.

Lischke, G. Ueber die Einwirkung von Cyankalium auf Chlorisocrotonsäureäthylester.

Mallmann, F. Beiträge zur Kenntniss des Chinins.

Mann, F. Orthoäthylmethylbenzol.

May, O. Ueber Azophtalsäure.

Müller, H. Ueber Methylderivate des Cinchonins.

Reiche, H. v. Ueber zwei Azodisulfobenzolsäuren und deren Derivate.

Reis, M. A. v. Zur Kenntniss der Oxalsäuren Salze, mit besonderer Rücksicht auf ihre Benutzung zur quantitativen Bestimmungen.

Rickmann, R. Beiträge zur Kenntniss der Constitution des Ultramarins.

Riebeck, E. Beiträge zur Kenntniss des Pyropissits.

Röhre, R. Beiträge zur Kenntniss des Brucins.

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